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Effect of ZnO seed layer on the catalytic growth of vertically aligned ZnO nanorod arrays

P.K. Giri\textsuperscript{a,b,*}, Soumen Dhara\textsuperscript{a}, Ritun Chakraborty\textsuperscript{a}

\textsuperscript{a} Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India
\textsuperscript{b} Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati 781039, India

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\textbf{A B S T R A C T}

We have grown vertically aligned ZnO nanorods and multipods by a seeded layer assisted vapor–liquid–solid (VLS) growth process using a muffle furnace. The effect of seed layer, substrate temperature and substrate material has been studied systematically for the growth of high quality aligned nanorods. The structural analysis on the aligned nanorods shows c-axis oriented aligned growth by homoepitaxy. High crystallinity and highly aligned ZnO nanorods are obtained for growth temperature of 850–900 °C. Depending on the thickness of the ZnO seed layer and local temperature on the substrate, some region of a substrate show ZnO tetrapod, hexapods and multipods, in addition to the vertically aligned nanorods. Raman scattering studies on the aligned nanorods show distinct mode at \( \sim 438 \text{ cm}^{-1} \), confirming the hexagonal wurtzite phase of the nanorods. Room temperature photoluminescence studies show strong near band edge emission at \( \sim 378 \text{ nm} \) for aligned nanorods, while the non-aligned nanorods show only defect-emission band at \( \sim 500 \text{ nm} \). ZnO nanorods grown without the seed layer were found to be non-aligned and are of much inferior quality. Possible growth mechanism for the seeded layer grown aligned nanorods is discussed.

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\section{1. Introduction}

ZnO nanostructures have attracted lots of interest due to its unique features such as wide band-gap (3.37 eV) and large exciton binding energy (60 meV) \cite{1,2} and wide applications in nanosize electronic, optics, sensors and optoelectronic devices \cite{3–6}. ZnO is one of the key materials in nanotechnology and nanosystems. ZnO have the capability to crystallize into many configurations resulting in diverse growth morphologies such as nanocrystalline films, rods, wires, springs, combs, belts, helixes, prisms, tetrapods, etc. \cite{7–15}. Several techniques have been used to grow ZnO nanowires. For example, thermal evaporation and condensation \cite{16}, metalorganic chemical vapor deposition (MOCVD) \cite{17} and molecular beam epitaxy (MBE) \cite{18} have been employed. Among them, the vapor–liquid–solid (VLS) deposition method involving the vapor-transfer process and thermal evaporation is the most frequently used method. For the production of high quality ZnO nanowires/nanorods, catalysts, such as Au, Cu and NiO, etc. \cite{19–21} have been most commonly used. The catalysts can improve the controllable growth of ZnO nanostructures. Catalyst free growth of only ZnO tripods \cite{22} or tetrapods \cite{15} has been reported. To our knowledge there was no such report on ZnO seed layer assisted growth of ZnO multipods (tetrapods and hexapods). Different groups have reported effect of ZnO seed layer for catalyst free growth of ZnO nanorods and its morphology, crystallinity and diameter by different methods \cite{23–25}. The crystalline quality of the ZnO seed layer strongly controlled the structural quality of the nanorods. In most of the cases synthesized nanorods were not aligned, hence have limited applications in nanosize electronic and optoelectronic devices. Therefore, it is crucial to have controlled and well aligned growth of ZnO nanorod arrays. Ultra thin layer and uniform distribution of ZnO seed in the ZnO layer are the key factors for well aligned vertical growth of ZnO nanorods. Zhao et al. have reported high temperature growth of vertically aligned ZnO nanorods on Si by with a thin ZnO seed layer \cite{26}. However, effects of growth temperature, substrate material and overall quality of the nanorods have not been studied. Here, we report the effect of pre-depositing ZnO seed layer on the structure, morphology and optical properties of gold catalytic grown vertically aligned ZnO nanorods arrays at different temperatures.

In this work, we have grown vertically aligned ZnO nanorods and multipods by a seeded layer growth techniques, using the VLS process. The effect of ZnO seed layer along with an Au catalyst layer and the growth temperature in the growth of vertically aligned ZnO nanorods are studied using structural and optical tools. Results are compared with the nanorods grown without the ZnO seed layer.

\* Corresponding author at: Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India. Fax: +91 361 2690762.
E-mail address: giri@iitg.ernet.in (P.K. Giri).
2. Experimental details

Vertically aligned ZnO nanorods were grown on Si substrates. Si(1 0 0) n-type doped substrate was first cleaned in trichloroethylene, acetone and methanol under ultrasonic bath for 15 min each to remove impurities and organic grease. The native oxide layer was etched out with buffered hydrofluoric acid solution. After each step, the substrate was rinsed with deionized water several times. Finally this was dried with N\textsubscript{2} gas blow. This substrate was used for VLS growth of vertically aligned ZnO nanorods by a three-step process. In the first step, a ZnO seed layer was deposited by RF-magnetron sputtering system. Sputtering was done at incident power of 100 W for 30 min at substrate temperature 300 °C. Argon and oxygen were used as reacting gases. In this process ∼3 μm thick ZnO seed layer was deposited on Si(1 0 0) substrate. In the next step, an ultra thin (∼50 Å) layer of gold was deposited by a mini sputtering system. The thickness of 50 Å for the Au layer was chosen for optimum growth of high quality nanorods. Finally, vertically aligned ZnO nanorod arrays have been grown by VLS process. In this process, a mixture of high purity ZnO powders (Sigma–Aldrich 99.999% purity) and high purity graphite powders (Fluka, 99.9%) at a weight ratio of 1:1 was used as a source. A quartz boat containing powder mixture was loaded in the central hot zone of 1000 °C. Inside a horizontal quartz tube, which is already placed inside the muffle furnace. The substrates are placed in downstream direction at various temperature zones (700–900 °C). Then furnace is ramped to 1000 °C and deposition was continued for 15 min with Argon gas flow rate 70 sccm (standard cubic centimeter mass). After deposition the entire system was cooled in room temperature and the synthesized product was taken for characterization. For comparison, growth experiment also performed at a substrate temperature of 800 °C on an Au coated Si substrate i.e. without predisposition of ZnO seed layer. To study the effect of substrate materials/orientation, similar experiments were performed on Au coated quartz substrate at 750 °C.

The as-grown ZnO nanorods were characterized with X-ray diffraction (XRD) (Bruker Advance D8, with CuK\textalpha\textsubscript{α} radiation), scanning electron microscopy (SEM) (LEO 1430VP), Room temperature photoluminescence (PL) measurements were performed with 325 nm laser excitation from a He–Cd Laser using a commercial fluorometer (LEO 1430VP). Raman measurements were performed with a 488 nm Ar ion laser excitation and a monochromator (Jovin-Yvon, Triax 550) in the back-scattering geometry. FTIR measurements were performed in the range 400–4000 cm\textsuperscript{-1} using a standard FTIR spectrometer (PerkinElmer, Spectrum BX).

3. Results and discussion

XRD is an ideal probe to characterize structure and orientation of thin film with respect to the substrate. XRD pattern of the as-grown ZnO seed layer is shown in Fig. 1(a) which reveals (0 0 2) oriented growth of the ZnO film. Fig. 1(b–d) shows the XRD spectra of the ZnO nanorods grown on Au coated ZnO seed layer at 900, 850 and 700 °C, respectively, while Fig. 1(e and f) shows the XRD patterns of ZnO nanorods grown at 800 and 750 °C without the seed layer on Si and quartz substrates, respectively. The nanorods grown with the seed layer show high crystallinity, the strong peak at 34.46° due to the ZnO(0 0 2) plane indicates the growth direction along c-axis of ZnO and is normal to the substrate plane. One strong (0 0 2) peak of hexagonal ZnO and small full width at half maximum (FWHM) value from the XRD pattern (Fig. 1(a–e)) indicates the c-axis of the single crystalline ZnO nanorods is well aligned and the growth direction is perpendicular to the base surface. Relative intensities of the XRD peaks in Fig. 1(a–f) show that nanorods grown at higher temperature have high value of peak intensity, which confirms higher crystallinity. The as-grown nanorods at 900 °C show small FWHM (0.0305°) and largest XRD peak intensity, which is ∼1.6 times higher than the XRD intensity of nanorods grown at 850 °C. And the nanorods grown at 700 °C (Fig. 1(d)) show large FWHM (0.0987°) and weak (0 0 2) peak intensity, which is ∼46 times smaller than the nanorods grown at 900 °C. XRD results clearly show that no preferential growth takes place for the growth of nanorods at 700 °C. Using Scherrer formula, we have calculated the diameter of the nanorods grown at 900, 850 and 700 °C, which are 273, 315 and 84 nm, respectively. We have found from XRD analysis that Au coating on ZnO seed layer induces a [1 1 1] orientation of the Au clusters at high temperature. The nanorods grown at 700 °C do not show preferential orientation, as evident from Fig. 1(d). Note that nanorods grown without the seed layer does not show any preferred orientation and possess inferior crystallinity as compared to that grown with seed layer. The additional peak of 43.1° in Fig. 1(e) is related to the graphite which is used during the VLS growth as a reducing agent. We have found that a substrate temperature below 800 °C is not favourable for the growth of (0 0 2) oriented nanorods by the VLS method. Note that previous study reported growth of aligned nanorods at 950 °C, which is relatively high [26].

Fig. 2(a–c) shows typical SEM morphology of ZnO nanorods grown on Au/ZnO/Si substrate at various growth temperatures. The nanorods grew in vertically on the substrate at 900 °C, as seen from Fig. 2(a). The inset in each case shows the magnified view of the aligned nanorods. The sizes of the nanorods are in the range of few
hundred nanometers and non-uniform diameters are due to vari-
ation in the local thickness of ZnO seed layer. ZnO seeds act as a
nucleation sites for the nanorods growth and importantly offers
very negligible lattice mismatch or almost mismatch free inter-
face between seed layer and nanorods, which results in the high
quality vertically aligned growth of ZnO nanorods arrays. Nanorods
grown at 900 and 850 °C (see Fig. 2(b)) have larger diameter and
highly aligned as comparable to the nanorods grown at 700 °C.
At high growth temperature, as the growth rate is high and ZnO
seed layer allows epitaxial growth process. Size control of these
nanorods can be accomplished by lowering gas flow rate, lower-
ing the growth temperature and deposited thinner ZnO seed layer
[24,25,27]. However, we found that lower substrate temperature
gives rise to high density of nanorods with not so aligned struc-
tures, as shown in Fig. 2(c). Fig. 2(d) shows the randomly oriented
ZnO nanorods which are grown at 800 °C without ZnO seed layer.
So ZnO seed layer have a strong effect on the aligned growth of ZnO
nanorods array. XRD analysis showed that nanorods grown with-
out seed layer are not c-axis oriented and have poor crystallinity. It
may be noted that ZnO deposited on Au coated quartz substrate at
750 °C does not show rod-like structure. It shows ZnO nanosilic-
ands of arbitrary shape. Thus, aligned nanorods could be grown only on
the crystalline Si substrates coated with ZnO seed layer, but not on
the quartz substrate.

Fig. 3(a–d) shows varieties of nanostructures formed at a fixed
substrate temperature (900 °C) on different locations of the Au
coated ZnO seed layer. Fig. 3(a) shows tetrapod and hexapod struc-
tures at the edge of the substrate that faces the source material.
Some of these have multipod structures and these are formed by
bunching of nanorods. Perhaps due to higher vapor pressure and
a relatively higher temperature at the source-facing edge of the
wafer (substrate), such hierarchical structures are formed at the
edge. Fig. 3(b) shows a side view of the ZnO nanorods and multi-
pods formed on the edge of the substrate, while Fig. 3(c) shows the
top view of the aligned nanorods with non-uniform diameters on
the flat surface of the substrate. Fig. 3(d) shows a tilted view of the
vertically aligned ZnO nanorods which are densely arrayed on the
Si substrate. Due to variation of local temperature on the substrate
and non-uniform diameter/thickness of the seed layer varieties of
nanostructures are formed on seeded layer even at a fixed substrate
temperature.

These nanorods are grown by typical VLS method, as the growth
temperature is above the eutectic temperature. Based on the above
results, it is understood that both gold and ZnO seed layer strongly
guided the growth orientation. So, for the Au/ZnO/Si substrate the
nucleation sites of ZnO nanorods have the same orientation as ZnO
thin film by the effect of the seed layer. The catalyst layer transfers
the orientation from seed layer to nanorods leading to a vertically
aligned growth [26]. For without ZnO seed layer, the nucleation
of ZnO on Au nanoislands is in random direction resulting non-
aligned nanorods. Here ZnO seed layer and Au layer together acting
as the nucleation site. By preparing ultrathin layer of ZnO and Au we
can synthesize small diameter ZnO nanorods. The growth of ZnO
tetrapods at higher temperature has been explained by octahedral
multiple twin (“octa-twin”) model [28–29], where centre nucleus is
considered as octahedral embryos is composed of eight pyramidal
crystals. However, the generalized growth model of multipods is
yet to be understood. Here multipods were grown only at higher
temperature. So during multipods formation, anisotropic surface
energy of different surface of hexagonal ZnO controls the bunching
of nanorods. And also concentration and energy of the Zn vapor has
strong effect on final shape of the nanostructures. So nucleation at

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**Fig. 2.** SEM images of seeded layer grown ZnO nanorods grown at different substrate temperatures (T_s): (a) 900 °C, (b) 850 °C, (c) 700 °C, (d) SEM image of non-aligned ZnO nanorods grown at T_s = 800 °C without any ZnO seed layer; (a and b) are shown in same scale. Inset in each figure shows the magnified view of the nanorods. Nanorods grown at 850 and 900 °C shows vertically aligned structures.
the initial stage has a crucial role on alignment and formation of different shape of the ZnO nanostructures.

The quality and suitability of the aligned nanorods in optical devices are further studied by PL and Raman studies. The room temperature PL emission spectra of the ZnO nanorods measured with 325 nm laser excitation are shown in Fig. 4. Fig. 4(a–c) is corresponding to the nanorods grown at 900, 850, 700 °C, respectively. The insets of Fig. 4(a and b) are the corresponding UV peaks in magnified scale. These show near band edge (NBE) UV emission peak ~380 nm, due to free excitonic recombination and defect related emission so called green emission band at ~498 nm which is attributed due to the recombination of photogenerated holes with the singly ionized oxygen vacancies [30]. Grabowska et al. [31] and Dai et al. [32] have also reported weak UV emission at room temperature from aligned ZnO nanorods. However, the UV emission becomes stronger than green emission at low temperature i.e. (7 K) [33]. But here we have observed comparable intensity of these two bands at room temperature from the nanorods grown at 700 °C. On the other hand, nanorods grown without the seed layer show no measurable intensity of UV emission, but a strong defect-emission band at ~502 nm, as shown in Fig. 4(d). For the aligned nanorods, the intensity of the UV peaks is increased with decrease in growth temperature. The lower intensity of NBE emission from vertically aligned nanorods is primarily due to the lower area of absorption by the tip of the aligned nanorods and corresponding emission. In case of non-aligned nanorods, the larger area of the nanorods surface enables higher absorption and corresponding higher emission intensity. It is also possible that the nanorods grown at higher temperature have larger oxygen vacancy and hence stronger visible emission band.

Fig. 5 shows the Raman spectra of the vertically aligned ZnO nanorods grown at different substrate temperature. All the spectra show $E_{2}^{high}$ Raman modes of ZnO at 438 cm$^{-1}$ corresponding to the wurtzite phase with varying intensities. Strong Si peak is coming

**Fig. 3.** SEM images of ZnO nanorods grown at 900 °C on different locations of the substrate: (a) SEM image of ZnO hexapods and multipods; inset shows the image of an isolated multipod. (b) SEM image of ZnO tripods, tetrapods at the edge of the substrate and side view of the vertically aligned nanorods at the front surface of the substrate. (c) Top view of the vertically aligned nanorods with non-uniform diameters, (d) tilted view (45°) of the dense array of vertically aligned ZnO nanorods on the ZnO seed layer.

**Fig. 4.** Room temperature PL spectra of seeded layer grown aligned ZnO nanorods deposited at various substrate temperatures ($T_s$): (a) 900 °C, (b) 850 °C, (c) 700 °C. (d) PL spectra of non-aligned ZnO nanorods grown at $T_s$ = 800 °C without any ZnO seed layer. Inset in (a) and (b) shows the enlarged view of the UV emission band.
Each case is due to the crystallinity of the vertically aligned nanorods. Treatment in the temperature range 500–800 °C improves crystallinity can be obtained by post-growth heat treatment in as-grown nanorods. Further cross-section due to larger area of exposure of the nanorods. Note nanorods, while the non-aligned nanorods have higher scattering cross-section due to lower area of scattering (cross-section) of the vertically aligned nanorods, which is consistent with the XRD results. Lower intensity of Raman signal from highly aligned nanorods arrays may be due to the lower area of scattering (cross-section) of the vertically aligned nanorods, while the non-aligned nanorods have higher scattering cross-section due to larger area of exposure of the nanorods. Note that these studies were performed on as-grown nanorods. Further improvement in crystallinity can be obtained by post-growth heat treatment in the temperature range 500–800 °C in oxygen/inert gas ambient.

FTIR studies on these samples confirmed the presence of Zn–O bonding modes in the as-grown nanorods. The FTIR spectra (not shown) of vertically aligned nanorods grown at 900 °C show absorption bands at 474 and 532 cm⁻¹, which correspond to the Zn–O bending mode and 525 cm⁻¹ corresponding to Zn–O stretching vibration mode of nanocrystalline ZnO, as Andres-Verges et al. calculated theoretically [34].

4. Conclusions

We have grown vertically aligned ZnO nanorods arrays possessing high crystallinity by a seeded layer growth process. The structural analysis on these nanostructures shows c-axis oriented aligned growth of ZnO nanorods. High crystalline quality and highly aligned ZnO nanorods are obtained for growth temperature of 850 and 900 °C. Lower temperature growth shows non-aligned nanorods. Depending on the thickness of the ZnO layer and local temperature, some regions of the substrate show ZnO tetrapods, hexapods, multipods in addition to the aligned nanorods. Raman scattering studies show distinct $E_{2}^{\text{high}}$ mode at 438 cm⁻¹, confirming the hexagonal wurtzite phase of the nanorods. The ZnO nanorods exhibit room temperature UV photoluminescence emission peak at ~378 nm, and a defect-emission band at ~498 nm. Nanorods grown without the seed ZnO layer shows non-aligned structures and have inferior structural and optical properties.

References