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<td><a href="http://hdl.handle.net/10220/12028">http://hdl.handle.net/10220/12028</a></td>
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Self-organized ZnO nanodot arrays: Effective control using SiNx interlayers and low-temperature plasmas


Citation: J. Appl. Phys. 111, 036101 (2012); doi: 10.1063/1.3673593
View online: http://dx.doi.org/10.1063/1.3673593
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v111/i3
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Additional information on J. Appl. Phys.
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Self-organized ZnO nanodot arrays: Effective control using SiN$_x$ interlayers and low-temperature plasmas


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(Received 8 November 2011; accepted 29 November 2011; published online 7 February 2012)

An advanced inductively coupled plasma (ICP)-assisted rf magnetron sputtering deposition method is developed to synthesize regular arrays of pear-shaped ZnO nanodots on a thin SiN$_x$ buffer layer pre-deposited onto a silicon substrate. It is shown that the growth of ZnO nanodots obeys the cubic root-law behavior. It is also shown that the synthesized ZnO nanodots are highly-uniform, controllable by the experimental parameters, and also feature good structural and photoluminescent properties. These results suggest that this custom-designed ICP-based technique is very effective and highly-promising for the synthesis of property- and size-controllable highly-uniform ZnO nanodots suitable for next-generation light emitting diodes, energy storage, UV nanolasers, and other applications. © 2012 American Institute of Physics. [doi:10.1063/1.3673593]

ZnO is an advanced metal oxide material with a wide direct band-gap of about 3.37 eV at room temperature and a large exciton binding energy of 60 meV. The exciton binding energy of ZnO (60 meV) is significantly higher than that of GaN (25 meV), which enables ZnO to emit short-wavelength light more efficiently even at room temperature. Recently, a broad range of deposition methods have been developed to prepare various ZnO nanostructures, such as nanowires, nanorods, nanobelts, nanorings, and nanorings. However, only a few research works have been focused on the preparation of zero-dimensional ZnO nanodots. Compared with one-dimensional nanostructures, zero-dimensional ZnO nanodots show a stronger exciton effect due to the three-dimensional quantum confinement. This leads to numerous applications of ZnO nanodots in short-wavelength optoelectronic devices such as UV light emitting diodes, UV nanolasers, as well as gas sensors, dye sensitized solar cells, and some other devices and systems.

In this work, a custom-designed, low-frequency (460 kHz), low-pressure, high-density inductively coupled plasma (ICP)-based deposition technique is used to synthesize regular patterns of highly-uniform pear-shaped ZnO nanodots. Moreover, we have systematically studied the growth dynamics of the synthesized ZnO nanodots and investigated the effect of the experimental parameters on the growth behavior of the ZnO nanodots through the use of a broad range of advanced analytical tools.

ZnO nanodots are grown on a thin SiN$_x$ buffer layer pre-deposited onto the (100) silicon substrate using an ICP-assisted rf magnetron sputtering deposition system. In this system, it is possible to control the plasma production and the sputtering independently. Prior to the deposition, the base pressure in the chamber of approximately 1.0 x 10$^{-3}$ Pa was achieved. After pre-evacuation, high-purity (99.99%) argon and hydrogen gases were let into the chamber at a rate of 9.6 and 3.2 sccm, respectively. The magnetron target used in this work is a high-purity (99.995%) stoichiometric ZnO (\([\text{Zn}] / [\text{O}] = 1.0\)). In addition, a thin SiN$_x$ buffer layer was deposited from a mixture of reactive argon, hydrogen, silane, and nitrogen precursor gases using the ICP-assisted chemical vapor deposition. The thickness of the SiN$_x$ buffer layer was approximately 30 nm.

A series of samples with different deposition times ranging from 10 to 40 min was prepared under a ZnO target power of 300 W, an inductive rf power of 1000 W, a substrate temperature of 450 °C, a ratio of the flow rates of the argon and hydrogen gases of 3:1, and a working pressure of 2.0 Pa. Figures 1(a)–1(d) show the top-view scanning electron microscopy (SEM) images of the samples with deposition times of 10, 15, 30, and 40 min, respectively. At a glimpse, one can notice the following features from the SEM images with the increase of the deposition time: (1) ZnO nanodots are uniformly distributed throughout the substrate; (2) the average size of the nanodots increases; (3) the density of the nanodots decreases; (4) the spacing between the nanodots increases. In order to further demonstrate that the ZnO nanodots are uniformly distributed throughout the substrate, the inset of Fig. 1 shows a typical size distribution of the ZnO nanodots with a deposition time of 30 min. One can notice that about 41% of the synthesized ZnO nanodots fall within the narrow range of 60-65 nm and the mean size is ~63 nm. Furthermore, our experiments reveal that at earlier growth stages the average size $d$ of ZnO nanodots follows the cubic root-law dependence on deposition time $t_D$ ($d \sim t_D^{1/3}$), which is consistent with the established theories of nanodot growth.
Another distinctive feature of the synthesized ZnO nanodots on the SiN\(_x\) buffer layer is revealed in the side-view SEM image. Figure 2 shows the tilt-view SEM image of the synthesized ZnO nanodots with a deposition time of 30 min. One can clearly observe that the densely packed spherical and pear-shaped structures with a large surface area to volume ratio are formed on the solid. These structures are arranged as if they do not wet the Si surface, which, to the best of our knowledge, has never been reported before for ZnO nanostructures.\(^6,7\)

Figures 3(a) and 3(b) show two typical SEM images of the ZnO nanodots deposited at substrate temperatures of 350 \(^\circ\)C (a) and 450 \(^\circ\)C (b), respectively, while the other experimental parameters remained the same. When the substrate temperature is increased from 350 to 450 \(^\circ\)C, the average size of the nanodot increases from 56 to 79 nm while the dot density significantly decreases from 3.33 \(\times\) 10\(^{10}\) to 1.76 \(\times\) 10\(^{10}\) cm\(^{-2}\). This result can be interpreted in terms of the classical nucleation theory. When the substrate temperature is low (350 \(^\circ\)C), the conditions for the high-density nucleation are favorable. Therefore, a large number of nucleation centers can be formed, which in turn leads to the high nanodot density.\(^1,17\) However, at a higher substrate temperature of 450 \(^\circ\)C, the diffusion and desorption rates of the adsorbed Zn and O atoms increase. The increase of diffusion rates leads to a large diffusion length, which in turn results in a large size and low density of ZnO nanodots at a higher substrate temperature of 450 \(^\circ\)C.

We have also investigated the influence of the inductive rf power on the growth of ZnO nanodots. Figures 3(c) and 3(d) show two typical SEM images of the ZnO nanodots deposited at inductive rf powers of 0 (without turning on the inductive rf power) and 500 W, respectively, while the other experimental parameters remained the same as before. Without turning on the inductive rf power, ZnO continuous films with quite small spacing between ZnO grains are formed (Fig. 3(c)). However, at an inductive rf power of 500 W, the uniform nanodots with a larger spacing can be obtained. This result can be interpreted based on the effect of the plasmas on the growth behavior of the ZnO nanodots. It is well known that the ICP source features high-density and highly-uniform plasmas.\(^18,19\) The electron number density obtained in the ICP plasmas can be approximately two orders of magnitude higher than that produced by the capacitively coupled plasmas under quite similar discharge conditions.\(^20,21\) With the addition of the ICPs, the density of reactive species can be significantly increased due to the strong interactions between the electrons and atoms. This increases the atom fluxes (Zn or O atoms) to the substrate due to the strong sputtering of the target and also the surface temperature due to the strong ion bombardment of the substrate surface. As a result, the surface diffusion length of Zn atoms increases, leading to larger nanodot sizes and inter-nanodot spacing.\(^14,22,23\)

Figures 4(a) and 4(b) show the typical narrow scan XPS spectra of the O 1\(_s\) and Zn 2p\(_{3/2}\) for the sample with a deposition time of 30 min. The peak fitting performed on the O 1\(_s\) spectrum yields two peaks, located at binding energies of 530.01 and 531.62 eV, respectively. These two peaks are...
attributed to O$^{2-}$ ions in the normal wurtzite structure of ZnO single crystal and O$^{2-}$ ions in the oxygen deficient regions within the matrix of ZnO.$^{1,24}$ Meanwhile, the Zn 2p$_{3/2}$ peak can only be fitted with one single peak, located at a binding energy of 1022.18 eV. This peak is attributed to Zn$^{2+}$ ions in the oxygen-deficient ZnO matrix, which suggests that Zn exists only in the oxidized state.$^{6,24}$ The relative atomic concentrations of Zn and O elements calculated by using the corresponding integrated peak areas and sensitivity factors (Zn: 2.768, O: 0.733) are 42.3 at % of O and 57.7 at % of Zn.$^{1,6}$

Fig. 4(c) shows the room temperature PL spectrum of the sample with a deposition time of 30 min. Two distinct peaks can be observed: one is sharp ultraviolet emission located at $\sim$387 nm, and the other one is broad green emission located at $\sim$550 nm. These two peaks are related with near-band-edge emission generated by free-excitation recombination and deep-level defect emission mostly generated by the single ionized oxygen vacancies.$^{1,25}$ As can be seen in Fig. 4(c), the ratio of the intensity of the UV peak to that of the green peak is very high, suggesting that the ZnO nanodots feature high quality and can be suitable for advanced optoelectronic and phononic applications.

If a thin SiN$_x$ buffer layer was not pre-deposited onto the silicon substrate, flat ZnO thin films without any nanodots were formed under quite similar deposition conditions. We believe that the thin SiN$_x$ buffer layer plays an essential role on the growth of these unusual pear-shaped ZnO nanodots. For example, it can change the interfacial energy between the substrate and the ZnO layer, and it can prevent the diffusion of Si atoms at a higher substrate temperature; moreover, the large lattice mismatch between ZnO and SiN$_x$ can promote the nanodot nucleation and growth.$^{5,21,26}$ The formation of the spherical shape of the ZnO nanodots can also be attributed to the influence of the SiN$_x$ buffer layer. Indeed, SiN$_x$ is a chemically very stable compound with the decomposition temperature of about 1900°C. Thus, establishing direct bonds between Zn and N is impossible at the process temperature used in our experiments. Therefore, the non-wetting behavior of ZnO is determined by the interfacial energy between ZnO and SiN$_x$. As our experiments show, a spherical shape of ZnO on SiN$_x$ is energetically preferred, due to the difference in the individual surface energies of the interfaced compounds. Indeed, it is known that the contact angle of SiN$_x$ is about 50°, whereas that of ZnO is about 90°$^*$–100°$^*$. Hence, the surface energies of these two compounds that form the interface are very different.

In summary, highly-uniform and size-controllable pear-shaped ZnO nanodots have been synthesized using ICP-assisted rf magnetron sputtering deposition system. Experimental results show that the growth of ZnO nanodots can be effectively controlled by the process parameters. X-ray photoelectron spectroscopy measurements show that the ZnO nanodots are oxygen deficient with 42.3 at % of O and 57.7 at % of Zn. Room temperature photoluminescence measurements demonstrate a dominant near-band-edge UV peak at $\sim$387 nm in the ZnO nanodots. These results are highly-relevant to the development of the next-generation light emitting diodes, UV nanolasers, solar cells, and other devices.

This work is partially supported by the National Research Foundation (Singapore), CSIRO’s OCE Science Leadership Scheme, the Australian Research Council (Australia), and the National Natural Science Foundation of China (Grant No. 90923005), Collaborations and fruitful discussions with X. X. Zhong are gratefully acknowledged.

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