Self-organized ZnO nanodot arrays : effective control using SiNx interlayers and low-temperature plasmas

Huang, S. Y.; Cheng, Q. J.; Xu, S.; Wei, D. Y.; Zhou, H. P.; Long, J. D.; Levchenko, I.; Ostrikov, K.

2012

Huang, S. Y., Cheng, Q. J., Xu, S., Wei, D. Y., Zhou, H. P., Long, J. D., et al. (2012). Self-organized ZnO nanodot arrays: Effective control using SiNx interlayers and low-temperature plasmas. *Journal of Applied Physics*, 111(3), 036101.

<https://hdl.handle.net/10356/97681>

<https://doi.org/10.1063/1.3673593>

© 2012 American Institute of Physics. This paper was published in *Journal of Applied Physics* and is made available as an electronic reprint (preprint) with permission of American Institute of Physics. The paper can be found at the following official DOI: <http://dx.doi.org/10.1063/1.3673593>. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Self-organized ZnO nanodot arrays: Effective control using SiNx interlayers and low-temperature plasmas

S. Y. Huang, Q. J. Cheng, S. Xu, D. Y. Wei, H. P. Zhou et al.

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>

Published by the [AIP Publishing LLC](#).

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT

The advertisement banner for AIP Advances features a green and yellow background with wavy lines. The AIP Advances logo is prominently displayed in the center, with a series of orange dots forming a curved path above the word 'Advances'. To the right, a circular seal states 'Now Indexed in Thomson Reuters Databases'. Below the logo, the text 'Explore AIP's open access journal:' is followed by a bulleted list of features.

AIPAdvances

Now Indexed in
Thomson Reuters
Databases

Explore AIP's open access journal:

- Rapid publication
- Article-level metrics
- Post-publication rating and commenting

Self-organized ZnO nanodot arrays: Effective control using SiN_x interlayers and low-temperature plasmas

S. Y. Huang,¹ Q. J. Cheng,^{2,3} S. Xu,^{1,a)} D. Y. Wei,¹ H. P. Zhou,¹ J. D. Long,⁴ I. Levchenko,^{2,3} and K. Ostrikov^{2,3}

¹Plasma Sources and Applications Center, NIE and Institute of Advanced Studies, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616

²CSIRO Materials Science and Engineering, Lindfield, New South Wales 2070, Australia

³Plasma Nanoscience @ Complex Systems, School of Physics, The University of Sydney, Sydney, New South Wales 2006, Australia

⁴Solar Energy Research Institute of Singapore (SERIS), National University of Singapore, Singapore 117574

(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 obey 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.^{1–4} Recently, a broad range of deposition methods have been developed to prepare various ZnO nanostructures, such as nanowires, nanorods, nanobelts, nanopins, nanorings.^{5–9}

However, only a few research works have been focused on the preparation of zero-dimensional ZnO nanodots.^{10–12} 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.^{10–12}

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.^{13,14} In this system, it is possible to control the plasma production and the sputtering independently.^{13,14} Prior to the deposition,

the base pressure in the chamber of approximately 1.0×10^{-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 ([Zn]/[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.^{15,16}

^{a)}Electronic mail: shuyan.xu@nie.edu.sg.

FIG. 1. (Color online) (a)–(c): Top-view SEM images of the samples with deposition times of 10 (a), 15 (b), 30 (c), and 40 (d) min, respectively. The inset shows a typical size distribution of the ZnO nanodots with a deposition time of 30 min.

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 and 450 °C with a deposition time of 40 min, respectively, while the other parameters remained the same. When the substrate temperature is increased from 350 to 450 °C, the average size of the nanodot increases from 56 to 79 nm while the dot density significantly decreases from 3.33×10^{10} to $1.76 \times 10^{10} \text{ cm}^{-2}$. This result can be interpreted in terms of the classical nucleation theory. When the substrate temperature is low (350 °C), the conditions for the high-density nucleation are favorable. Therefore, a large number of nucle-

ation centers can be formed, which in turn leads to the high nanodot density.^{1,17} However, at a higher substrate temperature of 450 °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 °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 1s and Zn 2p_{3/2} for the sample with a deposition time of 30 min. The peak fitting performed on the O 1s spectrum yields two peaks, located at binding energies of 530.01 and 531.62 eV, respectively. These two peaks are

FIG. 2. A typical tilt-view SEM image of the ZnO nanodots with a deposition time of 30 min (the left and right insets show zoom-in cross-sectional and tilted views of the pear-shaped structures, respectively). A shape close to spherical is clearly seen on the left inset.

FIG. 3. (a) and (b): Two typical SEM images of the ZnO nanodots deposited at substrate temperatures of 350 °C (a) and 450 °C (b), respectively; (c) and (d): Two typical SEM images of the ZnO nanodots deposited at inductive rf powers of 0 W (c) and 500 W (d), respectively.

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 ~ 387 nm, and the other one is broad green emission located at ~ 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 photonic 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°.²⁷ Hence, the surface energies of these two compounds that form the interface are very different.

FIG. 4. (Color online) (a) and (b): Typical narrow scan XPS spectra of the O $1s$ (a) and Zn $2p_{3/2}$ (b) for the sample with a deposition time of 30 min; (c): A typical room temperature PL spectrum of the sample with a deposition time of 30 min.

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 ~ 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. 90923 005). Collaborations and fruitful discussions with X. X. Zhong are gratefully acknowledged.

- ¹S. Li, X. Zhang, B. Yan, and T. Yu, *Nanotechnology* **20**, 495604 (2009).
- ²M. Xu, H. Zhao, M. Y. Duan, and L. X. Xu, *J. Appl. Phys.* **105**, 043708 (2009).
- ³K. Gao, W. Zhang, J. Sun, N. Xu, Z. F. Ying, Q. Li, J. Gan, and J. D. Wu, *J. Phys. Chem. C* **113**, 19139 (2009).
- ⁴M. Ghosh, R. S. Ningthoujam, R. K. Vatsa, D. Das, V. Nataraju, S. C. Gadkari, S. K. Gupta, and D. Bahadur, *J. Appl. Phys.* **110**, 054309 (2011).
- ⁵X. Zhong and X. Wu, *Plasma Processes Polym.* **6**, 161 (2009).
- ⁶Q. J. Cheng and K. Ostrikov, *Cryst. Eng. Comm.* **13**, 3455 (2011).
- ⁷M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, *Adv. Mater.* **13**, 113 (2001).
- ⁸K. Laurent, T. Brouri, M. C. Chichi, D. P. Yu, and Y. L. Wang, *J. Appl. Phys.* **110**, 094310 (2011).
- ⁹J. Shieh, F. J. Hou, Y. C. Chen, H. M. Chen, S. P. Yang, C. C. Cheng, and H. L. Chen, *Adv. Mater.* **22**, 597 (2010).
- ¹⁰M. K. Wu, Y. T. Shih, M. J. Chen, J. R. Yang, and M. Shiojiri, *Phys. Status Solidi (RRL)* **3**, 88 (2009).
- ¹¹K. K. Kim, N. Koguchi, Y. W. Ok, T. Y. Seong, and S. J. Park, *Appl. Phys. Lett.* **84**, 3810 (2004).
- ¹²K. Suzuki, M. Inoguchi, K. Kageyama, H. Takagi, and Y. Sakabe, *J. Nanopart. Res.* **11**, 1349 (2009).
- ¹³S. Xu, K. Ostrikov, J. D. Long, and S. Y. Huang, *Vacuum* **80**, 621 (2006); J. D. Long, S. Xu, J. W. Cai, N. Jiang, J. H. Lu, K. N. Ostrikov, and C. H. Diong, *Mater. Sci. Eng., C* **20**, 175 (2002).
- ¹⁴Q. J. Cheng, S. Xu, J. D. Long, and K. Ostrikov, *Appl. Phys. Lett.* **90**, 173112 (2007).
- ¹⁵C. J. Doss and R. Zallen, *Phys. Rev. B* **48**, 15626 (1993).
- ¹⁶Q. J. Cheng, J. D. Long, and S. Xu, *J. Appl. Phys.* **101**, 094304 (2007).
- ¹⁷L. M. Yang, Z. Z. Ye, Y. J. Zeng, W. Z. Xu, L. P. Zhu, and B. H. Zhao, *Solid State Commun.* **138**, 577 (2006).
- ¹⁸S. Xu, K. N. Ostrikov, Y. Li, E. L. Tsakadze, and I. R. Jones, *Phys. Plasmas* **8**, 2549 (2001).
- ¹⁹K. Ostrikov, *Rev. Mod. Phys.* **77**, 489 (2005).
- ²⁰I. Denysenko, M. Y. Yu, and N. A. Azarenkov, *Phys. Rev. E* **74**, 036402 (2006); S. V. Vladimirov, K. N. Ostrikov, M. Y. Yu, and L. Stenflo, *ibid.* **58**, 8046 (1998).
- ²¹U. Cvelbar, Z. Q. Chen, M. K. Sunkara, and M. Mozetič, *Small* **4**, 1610 (2008).
- ²²J. Zheng, R. Yang, L. Xie, J. Qu, Y. Liu, and X. Li, *Adv. Mater.* **22**, 1451 (2010).
- ²³A. Anders, *J. Phys. D: Appl. Phys.* **40**, 2272 (2007).
- ²⁴X. Q. Wei, B. Y. Man, M. Liu, C. S. Xue, H. Z. Zhuang, and C. Yang, *Physica B* **388**, 145 (2007).
- ²⁵C. V. Manzano, D. Alegre, O. C. Calero, B. Alén, and M. S. M. González, *J. Appl. Phys.* **110**, 043538 (2011).
- ²⁶J. H. Sun and H. C. Kang, *Thin Solid Films* **518**, 6522 (2010).
- ²⁷D. P. Subedi, D. K. Madhup, A. Sharma, U. M. Joshi, and A. Huczko, *Int. Nano Lett.* **1**, 117 (2011).