OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 11, November 2010, p. 1709 - 1712

Arc discharge assisted synthesis of ZnO whiskers and nanowires

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The last nanotechnology achievements and the variety of new phenomena following from the material dimension reduction have accelerated the study of nanoparticle properties and the methods of their production. This article reports synthesis of ZnO nanowires and nanowhiskers by the assistance of DC arc discharge. The arc is burned between a graphite cathode and a graphite anode filled with ZnO. The reactor operates in a pre-evacuated argon-filled chamber at a pressure of $3x10^4$ Pa. No catalysts have been used. ZnO of different morphology (nanowires, whiskers and particle agglomerates) is obtained on a Si wafer or on a glass substrate and has been studied by SEM and EDS.

(Received September 14, 2010; accepted November 10, 2010)

Keywords: ZnO nanowires, ZnO whiskers, Nanoparticles, ZnO evaporation

1. Introduction

ZnO is a well known material for years used in medicine, engineering and living standards. The interest of researchers has significantly grown in the last years with the rise of nanotechnology investigations and of the understanding that nanoparticles can have additional properties connected with size effects besides the ones characteristic for the bulk material. Scholars' efforts have been concentrated at searching efficient methods for such structure synthesis, studies on their properties and possibilities for their application. The most often used substrates on which nanostructures are deposited are glass and crystalline Si. When the aim is to obtain epitaxial layers, as well, right for the purpose are sapphire [1 and 2], GaN [3] and SiC [4].

The oxide exceptional properties make the nanostructures produced of it very suitable for applications in optoelectronic devices [5], sensors [6], highly efficient photonic devices [7], near-UV lasers [8], nanogenerators [9], aantireflective coatings (ARCs) [10], and electrochromic displays [11].

When aimed at producing structures of the same form, size and properties and grown perpendicular to the substrate resort to a preliminary deposition of Zn and Cu nuclei and of carbonized photoresists [12]. ZnO can be obtained of different morphology (nanowires (NWs) [13], nanobelts [14], tetra pods [15], nanocombs [16] and nanoneedles [17]), by different methods [18-20]. Various methods are applied to grow the layers: CVD [12], chemical methods [21], using carbonized photoresists to control the nucleation site, density, and growth direction of the nanowires [12].

2. Experiment

ZnO layer deposition is made in a stainless steel container (schematically shown in Fig. 1) by arc discharge with closely situated electrodes. The pure carbon (99.999) made electrodes are, correspondingly: an anode of cross section 10 × 10 mm^2 and length of 10 mm and a cathode of cross section 2 × 2 mm^2 and 40 mm length. The connected to a current source electrode ends are water cooled. Pure powdered ZnO is evaporated from an opening of 4 mm diameter, made on the anode, perpendicular to its longitudinal axe and at a distance of 1 mm from the arc zone. The container was evacuated to high vacuum and afterwards filled in with Ar to a pressure of 3×10^4 Pa. After the arc ignition by touching the electrodes, the distance between them is kept constant and equals 0.5 mm. The DC arc current was 75 A. Polished Si wafers of orientation 111 and glass are used as substrates. The later are fixed to a heater the temperature of which can be varied in the interval 20 – 600 °C.

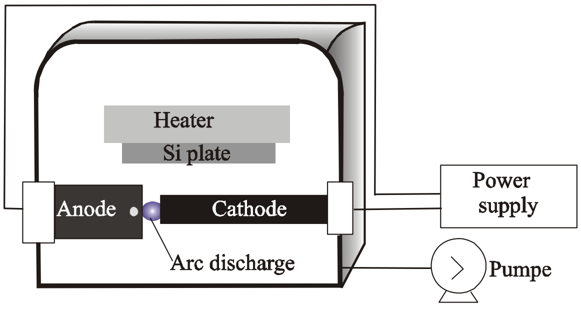

Fig. 1 Apparatus for nanowire and nanowhisker synthesis.

The obtained layers have been examined by SEM (Jeol-SEM JSM 6390) and EDS with no additional treatment.

3. Results and discussion

The arc process between closely located electrodes and at approximately equalized temperature is characterized by the fact that the electrodes are especially sized. During the arc process the cathode, normally, emits electrons which after leaving the surface take away some energy and transfer it to the anode. The later is heated and begins to sublimate. The cathode is cooled due to the electrons leaving and thus a substantial difference in temperature occurs sometimes reaching several hundreds of degrees. For the experiments discussed here a deteriorated heat transfer has been achieved at the cathode heating and bettered cooling of the anode by an appropriate selection of the electrode geometry and size. As a result electrode temperature equalization is realized at a value close to the carbon sublimation temperature. At that time electron thermal emission becomes enough to keep the arc burning. Under these conditions carbon sublimation is weak; the anode is not wearing out and that does not lead to an essential contamination of the carbon layers deposited. The inconsiderable carbon sublimation and the electrode high temperature make possible their usage as a heat source for evaporation of materials not fusing with carbon and having a point of evaporation lower than the one of carbon sublimation.

ZnO has a temperature of evaporation 2360°, it does not fuse with carbon and that allows ZnO layer to be deposited by this method, too.

A peculiarity of the considered way of ZnO deposition is the fact, that oxide vapours are moving in gaseous ambient (Ar pressure in the working chamber is $3\text{x}10^4$Pa) and they are partially decomposed. Due to collisions with the working gas molecules the oxide ones loose a part of their energy and reach the substrate with decreased kinetic energy. The kinetic energy with which molecules reach the substrate plays an important role for their migration on the surface and for building of the deposit structure. The substrate temperature has a significant contribution in the process of deposit formation morphology. The higher the temperature is and the lower the losses in collisions between the working gas and evaporated substance are, the more substantial that contribution is.

It has been established that ZnO deposition on a Si substrate at a temperature below 300 ^{o}C leads to an inconsiderable surface covering by small oxide clusters of increased Zn content. That indicates the substrate to be cool for the vapours reaching it, their migration over the surface is insignificant and they have no adhesion to it. The deposited layer is of a very low density. Because of the bigger adhesion forces among the oxide molecules themselves the material deposited unites in clusters of some tens of microns (Fig. 2). The saved in the molecules energy gives them an opportunity to arrange in nanowires of numerous defects. The later most often consist of very short strait parts of 0.3 – 1 μm length and diameters of 70 – 100 nm (Fig. 3). Such layers are appropriate for absorbers, catalysts and for antibacterial coatings for their large extended area. The poor adhesion is an important disadvantage.

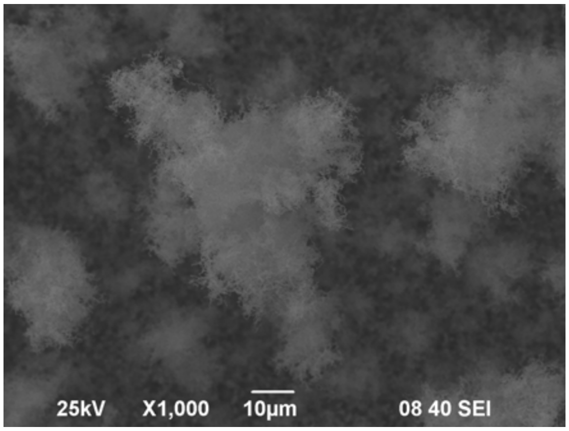

Fig. 2. Clusters in ZnO nanostructures.

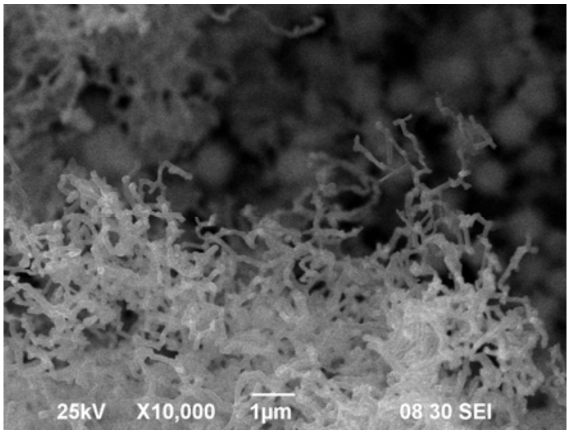

Fig. 3. ZnO nanowires on a substrate at 300^0C.

Rise of the substrate temperature above 300^0C increases the opportunity for ZnO molecule movement over the surface, capture in energetically favorable zones of the surface and, hence, formation of a denser and better caught to the substrate layer. Fig. 4 shows the cross section of such a layer and the whole surface is seen to be covered. Sizable is the congestion of the separate clusters. They are of dimensions of several hundreds of nanometers and they are monolithic. Nanowires are missing. A part of the clusters are in good thermal contact with the substrate and at a continuous flow of vapours they could serve as nuclei for building big size nanowires. Such nanowires grown on a substrate with a temperature of 400 ^{0}C are shown in Fig. 5. These nanowires follow the nucleus morphology and they are of various structures, sizes and properties. Different profiles of nanowires can be identified in Fig. 5: hexahedral, quadrangular and triangular ones.

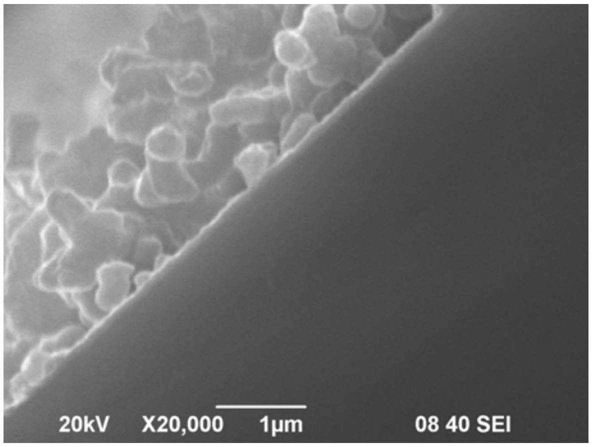

Fig. 4. Cross section of a layer deposited at 30 °C.

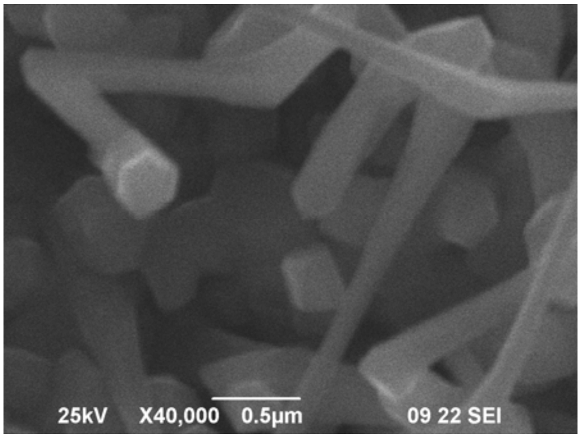

Fig. 5. ZnO nanowires grown from nuclei on the surface.

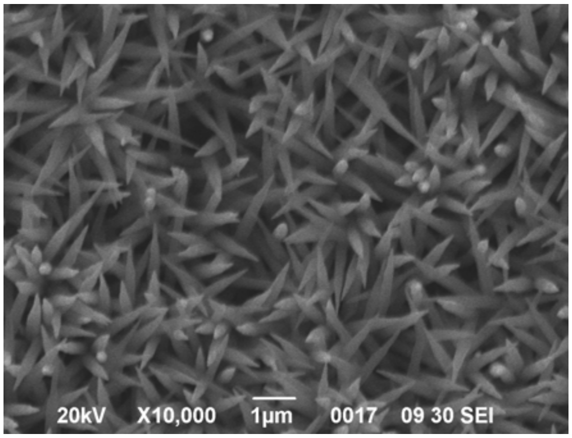

Fig. 6. Typical ZnO nanowire.

With the increase of substrate temperature to 600°C the conditions necessary for clusters on the surface to crystallize in the same way become more. This creates a premise the type, size and orientation of the growing up from them nanowires to be the same or very similar (Fig. 6). A great part of the nanowires are oriented in direction close to the perpendicular to the substrate. Structures of the kind are suitable for cold emitters and for solar cell electrodes.

When there is an intensive vapour flow there appear conditions for nuclei originating on the nanowire surface itself. That causes their repeated splitting and whisker growth. They shade the situated around nanowires and intensively grow on their account (Fig. 7).

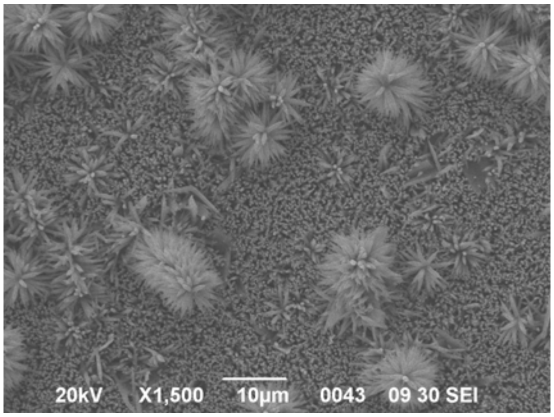

Fig. 7. ZnO whiskers orientation.

The significant influence of the substrate kind becomes apparent when glass is used as a substrate (Fig. 8). Then the adhesion is weaker than the one to Si substrate and, hence, nucleus origin is practically missing. Wires are growing almost in parallel to the surface, weakly connected to it and are several tens of microns long. The deposited layer density is very low.

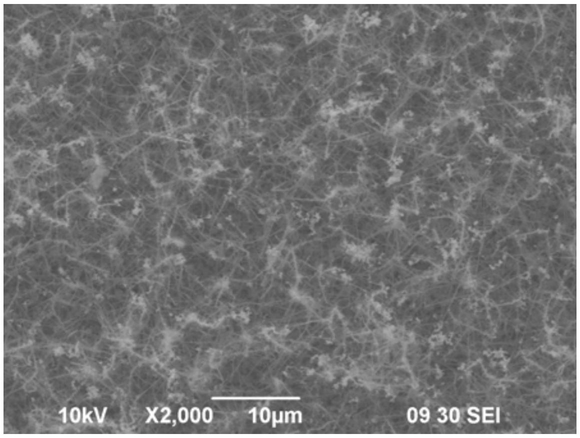

Fig. 8. ZnO nanowires on a glass substrate.

4. Conclusion

The obtained experimental data about ZnO layer and structure deposition on Si and glass substrates show that the substrate type and temperature are factors of substantial role for the growing particle morphology. That gives the possibility for various structures of high potentiality for different practical applications to be produced. The basic disadvantage of the prepared layers is their weak mechanical connection to the substrate. It might be an advantage in case the aim is not the preparation of oxide structure layers firmly bound to the substrate but just synthesis of structures in view of their application as individual components.

Acknowledgment

This work has been supported by the Bulgarian Science Foundation (contracts № DOO2-241 and № DOO2-207) which is gratefully acknowledged.

References

[1] X. D. Wang, Zhou, J. Song, J. H. Liu, J. Xu, N. Wang, Z. L., Nano Lett. **6**(12) 2768 (2006).
[2] X. D. Wang, J. H. Song, J. Liu, Z. L. Wang, Science, **316**, 102 (2007).
[3] X. D. Wang, J. H. Song, J. Liu, Z. L. Wang, Science **316**, 102 (2007).
[4] H. T. Ng, J. Han, T. Yamada, P. Nguyen, Y. Chen, P. Meyyappan, M. Single, Crystal Nanowire Vertical Surround- Gate Field-Effect Transistor, Nano Lett. **4**, 1247 (2004).
[5] W. S. Lee, M. C. Jeong, J. M. Myoung, Applications, Appl. Phys. Lett. **90**, 133115-1 (2007).
[6] X. D. Wang, J. Zhou, J. H. Song, J. Liu, N. Xu, Z. L. Wang, Nano Lett. **6**, 2768 (2006).
[7] M. A. Zimmler, D. Stichtenoth, C. Ronning, W. Yi, V. Narayanamurti, T. Voss, F. Capasso, Nano Lett. **8**, 1695 (2008).
[8] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H. J. Choi, Adv. Fun. Mater. **12**, 323 (2002).
[9] X. D. Wang, J. H. Song, J. Liu, Z. L. Wang, Science **316**, 102 (2007).
[10] Y. J. Lee, D. S. Ruby, D. W. Peters, B. B. McKenzie, J. W. P. Hsu, Nano Lett. **8**, 1501 (2008).
[11] X. W. Sun, J. X. Wang, Nano Lett. **8**, 18849 (2008).
[12] Ch. Cheng, M. Lei, L. Feng, T. L. Wong, K. M. Ho, K. K. Fung, M. T. Loy, D. Yu, N. Wang, High-Quality ZnO Nanowire Arrays Directly Fabricated from Photoresists, Publ. online 10.1021/nn800527m CCC: www.acsnano.org **3**(1), 53 (2009).
[13] P. J. Pauzauskie, P. Yang, Nanowire photonics, Materialstoday **9**(10), 36 (2006).
[14] X. Kong, Y. Ding, Z. Wang, J. Phys. Chem. B **108,** 570 (2004).
[15] Y. Dai, Y. Zhang, Q. K. Li, C. W. Nan, Chem. Phys. Lett **358,** 83 (2002).
[16] Y. S. Lim, J. W. Park, S.-T. Hong, J. Kim, Science and Engineering B **129,** 100 (2006).
[17] Y. Gui, C. Xie, Q. Zhang, M. Hu, J. Yu, Z. Weng, Journal of Crystal Growth **289,** 663 (2006).
[18] R. T. Kumar, J. Grabowska, J. P. Mosnier, M. O. Henry, E. McGlynn, Superlattices and Microstructures **42**, 337 (2007).
[19] Y. S. Fu, Y. F. Song, S. A. Kulinich, J. Sun, J. Liu, X. W. Du, Journal of Physics and Chemistry of Solids **69**, 880 (2008).
[20] M. Losurdo, M. M. Giangregorio, P. Capezzuto, G. Bruno, G. Malandrino, M. Blandino, I. L. Fragalà, Superlattices and Microstructures **38,** 291 (2005).
[21] P.-M. Chassaing, F. Demangeot, V. Paillard, A. Zwick, N. Combe, Phis. Rev. B **77**, 153306 1 (2008).

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