

Synthesis of Si and ZnO nanowires and whiskers by arc discharge*

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The dimension reduction of materials to a nanometer scale gives rise to several advantages. Crystalline nanostructures such as nanotubes and nanowires have received increasing attention due to potential applications in nanoscale electronics, optics, sensing devices and medicine. This article reports the synthesis of Si and ZnO nanowires and nanowhiskers by DC arc discharge using a graphite cathode and a graphite anode filled with a Si/C or ZnO/C powder mixture, respectively. The reactor operates in a pre-evacuated argon-filled chamber at a pressure of 3×10^{-4} Pa. The DC arc current was 75 A. No catalysts have been used. The material obtained has been studied by SEM.

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1. Introduction

The advantages of nanotechnology and the unique properties which some materials obtain by their size reduction have initiated intensive study of the phenomena causing those effects. The particle preparation methods, which determine the structures of the particles, their placement relative to one another, and their shape and size play important roles. Methods, developed so far, are able to produce a significant number of particles, which can work as active and passive electronic components, sensors and actuators. It is expected that the combination of these components with present electronics, microelectronics, instrument-building, measurement and medical techniques can improve their sensitivity, enlarge their operation possibilities and reduce their price. This explains the interest in the elemental and compound semiconductors such as Si, Ge, SiC, AlP, GaAs, GaN, BN, InP and ZnO.

In the last few years, a lot of carbon nanoparticles and new electronic components with remarkable properties have been developed. On the basis of the similarities between silicon and carbon, it is possible to expect that Si nanostructures can increase the number of these useful components and that they will be easy adapted to the Si electronics. Unfortunately, in contrast to carbon, Si has

preferential sp^3 hybridization. As result, Si tubular structures are unstable and difficult to fabricate.

ZnO is recognized as one of the most promising oxide semiconductor materials, due to its good optical, electrical and piezoelectric properties. Because of this, there is interest in its application in photonic devices [1], including laser and light-emitting diodes with low thresholds [2], optical waveguides and optical switches [3], sensors [4], solar cells [5], field emission sources and displays [6], piezoelectric devices, acousto-optic and surface acoustic devices [7]. Additionally, because ZnO can block 95% of UV radiation, it could be applied as a UV protective coating. It is used as a transparent highly conducting oxide, it has a stable field emission, it exhibits strong antimicrobial properties and ferromagnetism at room temperature.

ZnO can be obtained with different morphology (nanowires (NWs) [8], nanobelts [9], tetrapods [10], nanocombs [11] and nanoneedles [12]), by different methods [13].

In this work the preliminary results about preparation of Si and ZnO nanostructures by the method of arc discharge deposition is reported.

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2. Experimental

An arc discharge between closely situated carbon electrodes and a very low temperature gradient between them is employed to produce Si and ZnO nanostructures. This method is illustrated schematically in Fig. 1a. It has been initially developed for the production of carbon nanotubes. The cross-sectional area of the cathode is 6 mm². The anode, with a cross-sectional area of 12 x 10 mm, has two 4 mm openings, placed 1.5 mm apart (Fig. 1b). During the Si and ZnO sample preparation, both openings are filled with a mixture of Si crystals (~10 µm) or ZnO powder with a fine carbon powder, in the ratio of 90/10 wt %. The working atmosphere is pure Ar, with a pressure of 3x10⁻⁴ Pa. No catalyst or hydrogen for Si and ZnO nanostructure stabilization and stimulation are used in the experiment. The DC arc is ignited by touching the electrodes together and then separating them.

Si nanostructures are deposited on the surface of the anode material. In the case of ZnO, the nanostructures are deposited on c-Si substrates situated 10 mm below the electrodes, where the temperature is between 200°C and 400°C.

The deposited Si and ZnO materials have been studied by SEM (Jeol-SEM JSM 6390). The composition of the deposited structures has been studied by Energy Dispersive X-ray (EDX) spectroscopy.

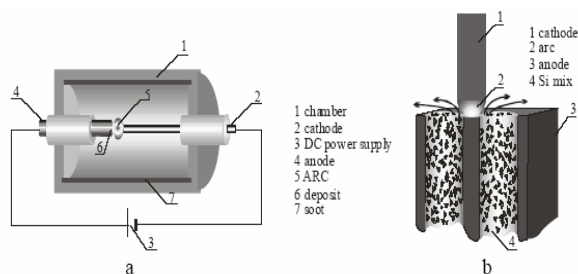


Fig. 1. (a) Schematic of the arc discharge apparatus and (b) the cross-section of the anode.

3. Results and discussion

In the case of DC arc discharge between closely situated carbon electrodes, the temperature of the anode was higher than that of the cathode, due to the energy transport caused by electrons emitted from the latter. This increased the carbon sublimation, which took place on the anode. In the method used here, the temperatures of two electrodes were kept almost equal, by water cooling of the anode and heating the cathode. Water-cooling and a bigger cross-section of the anode were employed to reduce its temperature and to prevent sublimation. In contrast, a small cathode diameter increased its temperature, enlarging through that its thermo electron emission and affecting its very weak sublimation. After ignition, the arc was situated between the cathode and the part of the anode that is between the openings. This was caused by the high electrical resistance of the Si/C or ZnO/C mix. In the

openings, where Si was placed, the temperature fell linearly from 3000 to 1600 °C. Si has a melting point of 1414 °C and a boiling point of 2900 °C at atmospheric pressure. However, the boiling point depends on the pressure and at our working pressure it was lower than 1900 °C. Due to the temperature distribution in the opening, higher than the Si melting point, it can be expected that during the arc discharge all Si particles will melt. To separate the drops of molten Si in the opening and to evaporate only those Si drops that are near the arc, we used a mix of Si particles and carbon powder. The big difference in the evaporation temperature of Si and C caused a noticeable excess of Si atoms in the vapor flux.

The surface of the anode was greater than the arc diameter (Fig. 1b), which resulted in a temperature reduction, reaching 1100 °C on the

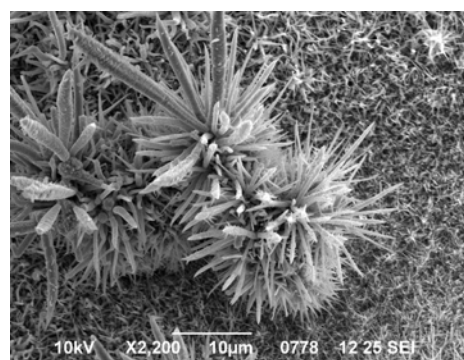


Fig. 2. SEM of the Si whiskers.

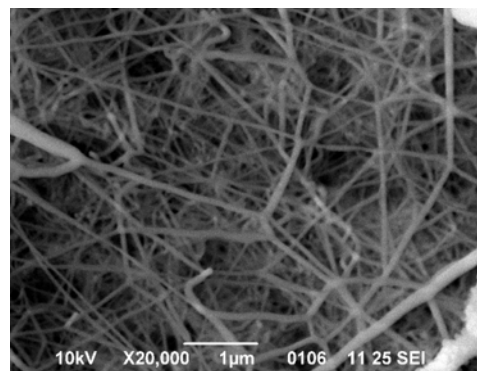


Fig. 3. SEM of the splintered Si nano-wires.

periphery. This temperature was lower than the condensation temperature of Si. Therefore, all conditions for the deposition of material on the surface of the anode were fulfilled. The particles deposited on the edges of the openings and on protruding places had shapes similar to those shown in Fig. 2. These whiskers had lengths of up to 20 µm and diameters up to 3 µm. Their Si nature was established by Energy Dispersive X-ray spectroscopy.

We also observed almost uniform Si nanowires under and around the whiskers (Fig. 2). These had diameters from 0.03 to 0.3 µm and lengths from 0.3 to 5 µm. They contained up to 10,000 times less material than the

whiskers, due to the much lower supply of material in that region.

Splitting of the growing Si crystals frequently occurred - some of the nanowires changed their directions or branched out several times during their growth (Fig. 3).

The proposed method for ZnO particle synthesis did not use catalysts like Zn and Cu during the process, either in the powder mixture or deposited on the substrate. ZnO has a melting temperature of 1975 °C. This is lower than the temperature which the ZnO/C mix could obtain during the arc burning. The ZnO did not melt with the carbon from the mix and from that on the open walls. It was evaporated intensively and reached the Si substrate or the particles grown on it maintaining its high energy. This increased the molecule migration on the surface and stimulated the growth of ordered structures. Fig. 4 shows a part of the substrate area covered with a perfect column of ZnO. It has to be noted that the Si substrate was not handled previously and had not deposited seeds (like Au [14]) on its surface. EDX spectroscopy estimated the Zn/O ratio of the atoms to be 55/45, which did not correspond to the ZnO stoichiometry. On the basis of this, it is possible to suppose that ZnO in the powder mixture was decomposed partially during the evaporation and the Zn concentration on the top of the growing particles increased. Probably this has caused a vapor liquid solid (VLS) deposition to some extent, and has resulted in a well ordered column structure. The diameter of the columns was in the range of 200 – 300 nm and their length was several micrometers. These columns were big as a result of the intensive vapor flux of molecules with high kinetic energy. The covering of large areas with homogenous columns is also valuable for their application as gas sensors and for medical purposes, due to their very large active surface.

In the zone where the temperature is lower and thermal contact between the substrate and the growth particles is poor free standing wires start growing. They are up to 10 µm long and with diameters of 50-150 nm (Fig. 5).

In the same lower temperature zone when the vapour flux become more intensive the defected particles rise and act as a seeds for growing of splitting wires (a growth of the wires into several directions) (Fig. 6).

In the growing area where the temperature is low (about 200°C) the rate of molecule migration is also lower. In these conditions, the number of ZnO defect nanoparticles rises. The low rate of molecule migration stimulates the growth of the whiskers, as well (the needles look like cones and are pointed in different directions). At the end of the process of synthesis, they look like cacti (Fig. 7). The agglomerate of whiskers has a big cross section to the vapor flux and thus has received a large quantity of molecules. Due to the low temperature where the whiskers start growing, molecule migration to the needle top becomes more difficult. In this case, the enlargement of the needles is due only to the high kinetic energy of that the vapor molecules possess.

The difference in the growth mechanism of the particles in the samples results in changes of the size of the

nanostructures in the deposited ZnO material. The nanowires in the whisker structured ZnO (Fig. 7) have lower diameter size (100-200 nm) than the columns in the samples shown in Fig. 4 (200-300 nm) and as a consequence larger effective area. The estimated by EDX spectroscopy Zn/O ratio in the nanowhiskers which SEM is shown in Fig. 7 was 41/50. It is possible to assume that the observed deviation from the stoichiometry of the ZnO with the whiskers structure is caused by the water vapor absorption from the ambience during the time between the preparation and the EDX measurement.

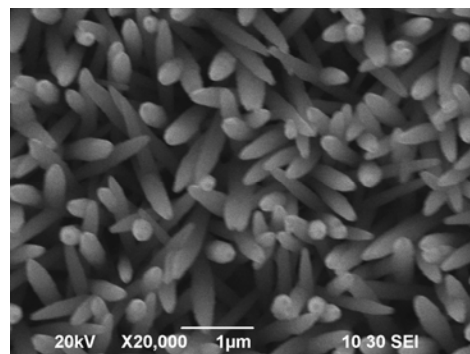


Fig. 4. SEM of the samples with column ZnO morphologies

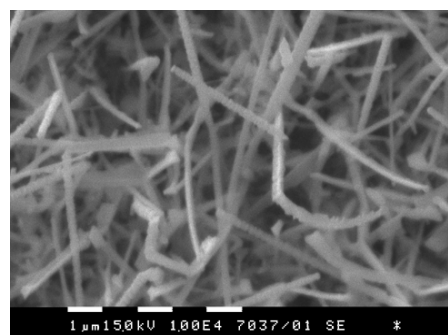


Fig. 5. A network of free-standing ZnO wires

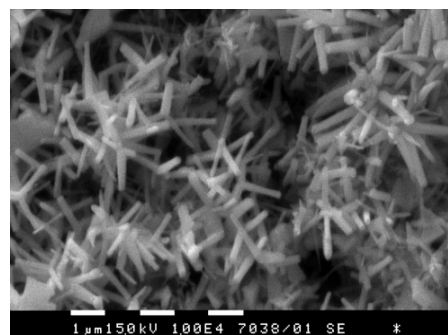


Fig. 6. Splintered wires

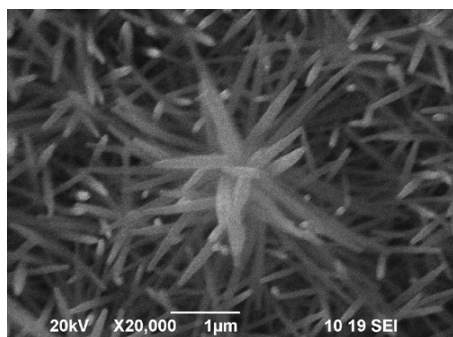


Fig. 7. ZnO nanowhiskers.

4. Conclusions

A DC arc discharge, employed initially for the fabrication of CNT, was successfully used to create

Si and ZnO nanostructures. A SEM study of Si material deposited on the surface of the anode showed that the conditions realized were adequate to allow the growth of whiskers and nanowires without the use of catalysts. The whiskers were observed near the anode openings and on protruding places. Nanowires appeared beyond the whisker regions, in areas with a lower temperature and flux. The mixture of small Si crystals and C powder prevented the intensive formation of SiC in the anode openings.

The growth of well ordered ZnO columns on Si substrates, free-standing ZnO nanowires and whiskers was realized without catalysts and substrate handing. The possibility for covering large areas with perfect ZnO tips is important for the use of such morphologies as field emitters of electrons, in gas sensors and for medical applications. The growth mechanism of the ZnO columns and of the whiskers was different which resulted in changes of the size of the nanostructures in ZnO samples and their stoichiometry.

References

- [1] J.-F. Yan, Y.-M. Lu, H.-W. Liang, Y.-Ch. Liu, B.-H. Li, Xi-Wu Fan, J.-M. Zhou, *J. Cryst. Growth* **280**, 206 (2005).
- [2] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, *Adv. Mater.* **13**, 113 (2001).
- [3] A. B. Djuricic, Y. H. Leung, *Small* **2**, 944 (2006).
- [4] Z.-P. Sun, L. Liu, L. Zhang, D.-Z. Jia, *Nanotechnology* **17**, 2266 (2006).
- [5] R. E. I. Schropp, H. Li, R. H. Franken, J. K. H. Rat, C. H. M. Van der Werf, J. W. A. Schüttauf, R. L. Stolk, doi:10.1016/j.tsf.2007.12.089 (2008).
- [6] Y. Zhang, Y. Huang, J. He, Y. Dai, S. Wang, C. Zhou, *Mater. Res. Soc. Symp. Proc.* **879** E, 771 (2005).
- [7] J. Song, X. Wang, J. Liu, H. Liu, Y. Li, Z. Wang, *Nanoletters* **8**, 203 (2008).
- [8] P. J. Pauzauskie, P. Yang, *Nanowire photonics*, *Materials Today* **9**, 36 (2006).
- [9] X. Kong, Y. Ding, Z. Wang, *J. Phys. Chem. B* **108**, 570 (2004).
- [10] Y. Dai, Y. Zhang, Q. K. Li, C. W. Nan, *Chem. Phys. Lett.* **358**, 83 (2002).
- [11] Y. S. Lim, J. W. Park, S.-T. Hong, J. Kim, *Mat. Sci. Engineering B* **129**, 100 (2006).
- [12] Y. Gui, C. Xie, Q. Zhang, M. Hu, J. Yu, Z. Weng, *J. Cryst. Growth* **289**, 663 (2006).
- [13] H. Chenga, J. Chengb, Y. Zhangb, Q.-M. Wanga, *J. Cryst. Growth* **299**, 34 (2007).
- [14] E. Greyson, Y. Babajan, T. Ododm, *Adv. Mater.* **16**, 1348 (2004).

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