Formation mechanisms of metallic Zn nanodots by using ZnO thin films deposited on n-Si substrates

J. M. Yuk, J. Y. Lee, Y. Kim, Y. S. No, T. W. Kim, and W. K. Choi

1Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea
2Max Planck Institute of Microstructure Physics, D-06120 Halle (Saale), Germany
3Department of Electronics and Computer Engineering, National Research Laboratory for Nano Quantum Electronics Devices, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea
4Thin Film Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

(Received 13 January 2010; accepted 12 July 2010; published online 9 August 2010)

High-resolution transmission electron microscopy and energy dispersive x-ray spectroscopy results showed that metallic Zn nanodots (NDs) were fabricated through transformation of ZnO thin films by deposition of SiOx on ZnO/n-Si (100) heterostructures. The Zn NDs with various sizes and densities were formed due to the occurrence of the mass diffusion of atoms along the grain boundaries in the ZnO thin films. The fabrication mechanisms of metallic Zn NDs through transformation of ZnO thin films deposited on n-Si substrates are described on the basis of the experimental results. © 2010 American Institute of Physics. [doi:10.1063/1.3475016]

A nanodot (ND), which is referred to a nanometer-sized zero-dimensional structure, exhibits unusual electrical and optical properties because of three-dimensional quantum confinement effects.3,4 NDs are of current interest because of their potential applications in nanoelectronic devices, such as single-electron transistors,5-6 lasers,7-10 light-emitting diodes,11-14 and photovoltaic cells.15-18 NDs are significantly smaller than structures used in current microelectronic devices, making it difficult to form NDs using standard lithographic techniques. NDs have been extensively formed using the Stranski–Krastanov (SK) island growth method.15 This method is self-assembly growth resulting from the release of the strain energy accumulated by the lattice constant difference between the deposited material and the substrate. However, the kinetics of the SK island growth for the NDs depend on several factors, such as the initial thickness of the film, the relative rate of adatom attachment during vapor deposition, the relative rate associated with the surface diffusion, the competition between the strain and the surface energies, their associated anisotropies, and the wetting layer thickness.20 These factors might restrict the determination of ND and substrate materials. Therefore, an alternative method is required for the fabrication of various NDs on diverse substrates. Even though the SK growth method has been extensively employed as means of artificial ND formation, studies concerning the precise control of the size and the density of the NDs by using a simple process have not yet been performed.

This letter reports data for the fabrication mechanisms of metallic Zn NDs through transformation of ZnO thin films deposited on n-Si substrates by using radio-frequency (rf) magnetron sputtering. High-resolution transmission electron microscopy (HRTEM) measurements were carried out to identify NDs and to investigate their microstructural properties. Energy dispersive x-ray spectroscopy (EDX) measurements were performed to characterize the composition of the NDs and the matrix. The fabrication mechanisms of metallic Zn NDs through transformation of ZnO thin films deposited on n-Si substrates are described on the basis of the experimental results.

The sample preparation process for the fabrication of Zn NDs is shown as a schematic diagram in Fig. 1. In the first preparation step of Fig. 1(a), 5 and 10 nm-thick ZnO thin film with polycrystal columnar structures shown in the cross-sectional bright-field TEM image were deposited on n-Si (100) substrates. Polycrystalline stoichiometric ZnO with a purity of 99.999% was used as a source target material and was precleaned by repeated sublimation. The carrier concent-

![Image](https://via.placeholder.com/150)

FIG. 1. (Color online) Schematic diagram illustrating the preparation process of the Zn NDs: (a) the deposition of 5 and 10 nm ZnO thin films on n-Si (100) substrates and the corresponding cross-sectional bright-field TEM image, (b) the sputtering of the SiOx layers with the same thicknesses as ZnO thin films onto the ZnO/n-Si heterostructures, and (c) the transformation from the ZnO thin films to the Zn NDs embedded in SiO2 matrix.
tration of the P-doped n-Si substrates with (100) orientations used in this experiment was $1 \times 10^{15}$ cm$^{-3}$. The substrates were degreased in trichloroethylene (TCE), rinsed in de-ionized water, etched in a mixture of HF and H$_2$O (1:1) at room temperature for 5 min, and again rinsed in TCE. After the Si wafers were chemically cleaned, they were mounted onto a susceptor in the growth chamber. After the chamber was evacuated to $8 \times 10^{-7}$ Torr, the deposition was done at a substrate temperature of 300 K. Ar gas with a purity of 99.999% was used as the sputtering gas. Prior to ZnO growth, the surface of the ZnO target was polished by Ar$^+$ sputtering. The ZnO deposition was done at a system pressure of $5 \times 10^{-3}$ Torr and an rf power ($rf=13.26$ MHz) of 100 W. A gas flow of Ar was 5 sccm and the growth rate was approximately 1.17 nm/min. Subsequently, SiO$_2$ layers with the same thicknesses of ZnO thin film were deposited onto the ZnO thin film under the same conditions as a deposition of the ZnO thin film. From the diffused epoxy or some organic contamination generated during the sample preparation procedure, O and Si atoms were detected at the 1 circle and Zn, O, and Si atoms were detected at the 2 circle. This result indicates that the formation of Zn NDs originates from the subsequent process of SiO$_2$ deposition on the ZnO thin films. The deposited or the reacted ZnO and SiO$_2$ layers do not always contain stoichiometric oxygen contents. This results in the occurrence of the substoichiometric oxide layers. When the sputtered Si atoms could not make a bonding with O atoms, they might collide with the ZnO surface, resulting in the breaking bonding of ZnO. The Si atoms can be oxidized into the thermodynamically more stable SiO$_2$ because the free energy for the formation of the SiO$_2$ layer at $\sim 300$ K ($G_f^0 = \sim -210$ kcal/mol) is much larger than that of the ZnO layer ($G_f^0 = \sim -161$ kcal/mol). The oxidation rate of Si atoms is basically much higher than that of the metals at room temperature because the single-bond strength between Si atoms (42 kcal/mol) is lower than that between almost of metal atoms. The formed SiO$_2$ is very stable at room temperature because the single-bond strength of SiO$_2$ (106 kcal/mole) is much stronger than that of the metal oxide.

To observe a transformation process of the ZnO thin film into the Zn NDs, the SiO$_2$ layer with a thickness of 5 nm was deposited on the ZnO thin film with a thickness of 30 nm. The dotted lines indicate grain boundaries.

FIG. 2. (Color online) (a) A cross-sectional bright-field TEM image of hemispheric Zn NDs embedded in a SiO$_2$ matrix. (b) An enlargement of the part of (a). (c) HRTEM image of the Zn ND with a zone axis along the $[\bar{2}\bar{1}\bar{0}]$ direction and the corresponding FFT electron-diffraction pattern (insets). EDX point spectra taken from the numbers (d) 1 and (e) 2 in circled areas of (b).
of atoms occurred along the grain boundaries of polycrystalline thin films, it could be possible to precisely control the sizes and the densities of Zn NDs. The present observations can help improve our understanding of the mechanisms on the transformation from metal oxide thin films to metallic NDs.

The authors would like to thank Dr. Youn-Joong Kim at the Korea Basic Science Institute. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MEST) (No. 2010-0018877), and this work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) Grant No. 2009-0094040.

FIG. 4. (Color online) Plane-view bright-field TEM images of Zn NDs with average radii of (a) 5 and (b) 10 nm.