Self-assembled zinc oxide nanodots on silicon oxide

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Abstract. Self-assembled ZnO nanodots are grown by electron beam evaporation of Zn on thermally oxidized silicon substrates and subsequent annealing in oxygen. Characterization by TEM and EELS shows that the quantum dots are indeed zinc oxide single crystals grown with their c-axis perpendicular to the substrate; their distribution and size depends on the deposition parameters of zinc onto the substrates.

1. Introduction
Zinc oxide is a semiconductor with interesting and versatile properties [1] which may find applications in optoelectronics, spintronics, transparent electronics and gas sensing. Recently, the promise for the application of ZnO in nanoscale optoelectronics has led to the development of several methods for the growth of wire-like ZnO structures. Vapor phase transport has been used for the growth of ZnO nanowires on Au coated silicon and NiO catalyzed Al2O3 substrates [2,3] and MOCVD and CVD for the growth ZnO nanorods on clean silicon substrates [4,5]. Nanobelts and nanorings of ZnO have also been grown by ZnO powder evaporation in argon atmosphere [6, 7]. On the other hand, less work has been reported on ZnO nanoparticle formation [8,9,10] and even less on their growth on silicon substrates [11].

In this paper we report the growth of ZnO quantum dots by electron beam evaporation of Zn on thermally oxidized silicon substrates and subsequent annealing in oxygen. This method is compatible with Si based device fabrication processes and therefore can be used in incorporating ZnO quantum dots in such devises.

2. Experimental details
Zn metal, 99.99% pure, was evaporated by electron beam heating in a vacuum of 4x10^-8 Torr on thermally oxidized (100) Si. The substrate temperature was varied from 200 to 300 K by liquid nitrogen cooling; the rate of evaporation varied between 0.05 to 0.6nm/s and the total Zn deposited was equivalent to layer thicknesses between 1 and 2nm. The rate of evaporation and total thickness were measured by a quartz crystal monitor, kept at 300K during evaporation by water cooling. The samples, after warming up to RT, were transferred to an oven where they were annealed at 570K for one hour in a flow of oxygen.

Initial experiments showed that during Zn deposition, at substrate temperatures near 300K and above, Zn re-evaporated from the substrate completely, rendering the growth of nanoparticles or thin continuous layers impossible. This behavior of Zn on SiO2 substrates is in agreement with its behavior on crystalline alumina [12], where it shows a very low sticking probability even at 250K, dictated to us the necessity to work at low substrate temperatures. Furthermore, it raises some questions about the
certainty of the measurement of the rate of evaporation by the quartz crystal monitor, since the
sticking probability of Zn onto the gold covered quartz crystal at 300K is not known.

The samples were examined before and after oxidation by Transmission Electron Microscopy
(TEM), in order to determine their morphology and structure, and by Electron Energy Loss
Spectroscopy (EELS) in order to determine their chemical composition. The TEM studies were carried
out with a Philips CM20 electron microscope equipped with a Gatan GIF200 energy filter.

3. Results and discussion

Figure 1 shows a TEM image of the plan view of nanoparticles grown on thermally oxidized Si
substrate. The Zn evaporation was carried out at a rate of 0.3nm/s, the total Zn deposited was
equivalent to a layer of 1nm in thickness and the substrate temperature was 210K. Oxidation of the Zn
nanoparticles was carried out in oxygen flow at 570K for one hour. The nanoparticles formed, are of
irregular shape with an average size of approximately 20nm and their density is approximately
6x10^{10} \text{cm}^{-2}. The nanoparticles, before and after oxidation, have the same morphology and distribution,
but oxidation increases their size. Electron diffraction showed that the nanoparticles are crystalline
with d-spacing values equal to those of bulk ZnO, indicating that during the thermal treatment in
oxygen the Zn nanoparticles were transformed to ZnO. The fact that the electron diffractogram, shown
as inset in figure 1, consists of rings corresponding to the ZnO crystalline
planes (2\overline{1}T0), (11\overline{2}0), (4\overline{2}20) and (10\overline{1}0) only, indicates that the nanoparticles have their a and b
axes randomly oriented and their c-axis perpendicular to the substrate. This high degree of c-axis
orientation is rather common in ZnO even when grown on amorphous SiO_2 [13,14]. High Resolution
TEM (HRTEM) study of the sample, inset of figure 1, confirms this high degree of c-axis orientation
and furthermore, it shows that the ZnO nanoparticles are single crystals, although some of them contain defects.

![Figure 1. TEM plan view of ZnO nanoparticles on thermally oxidized Si substrate. The Zn evaporation was carried out at a rate of 0.3nm/s the total Zn deposited was equivalent to a layer of 1nm in thickness and the substrate temperature was 210K. Oxidation of the Zn nanoparticles was carried out in oxygen flow at 570K for 1h. Insets show an electron diffraction pattern of nanoparticles and a HRTEM view of a single nanoparticle.](image)

The shape, size and distribution of the nanoparticles on the substrate can be varied by changing the Zn
deposition parameters i.e. the substrate temperature, the rate of deposition and the total thickness. As
an example of the effect of deposition rate on the morphology of the nanoparticles we show in figure 2
a plan view image of ZnO nanoparticles grown at 210K with an evaporation rate of 0.6nm/s, a total
thickness of deposited Zn equivalent to a layer of 1nm in thickness and the substrate temperature was 210K.
Oxidation of the Zn nanoparticles was carried out in oxygen flow at 570K for 1h. This sample was grown at the same conditions as that presented in figure 1, but with twice the deposition rate. As can be seen in figure 2, the average size of the ZnO particles is larger, approximately 35nm, and their density is almost half, 3.5x10^{10} \text{cm}^{-2}. However, the particles are no longer single crystals but agglomerates of small crystallites. We note that theoretically [12], we expected that the increase of the
deposition rate should have caused an increase in the density of the particles. We believe that this
unexpected result indicates that the adatom surface mobility of Zn on the SiO_2 surface is so large, even
at such a low temperature, which allows fast agglomeration of the smaller particles into larger ones.
resulting in an apparent decrease of their density. On the other hand, an increase of the substrate temperature to 260K, results in an increase of the size of the ZnO nanoparticles up to 70nm, as shown in plan view in figure 3. We note, however, that at this temperature the re-evaporation of Zn from the substrate is large and, in order to achieve formation of nanoparticles, we had to deposit Zn equivalent to a layer of 2nm in thickness. A cross-section view of these nanoparticles is shown in figure 4. Their lateral dimensions are those determined by the plan view in figure 3, while their height varies from 5 to 15nm. The inset of figure 4 shows one of the nanoparticles (HRTEM) verifying that it is a single crystal, grown with its c-axis perpendicular to the substrate.

In order to examine further the chemical composition of the nanoparticles, some of them were scraped off the SiO2 substrate and transferred in ethanol solution onto carbon coated TEM grids for EELS experiments. For comparison purposes, similar samples were prepared with ZnO powder of 99.9995% purity. Figure 5a shows the EELS spectrum of the O-K edge of the ZnO nanoparticles and powder, while figure 5b shows their Zn-L edge. The similarity of the two sets of spectra proves that the nanoparticles are ZnO in agreement with the electron diffraction results presented above, as well as, with other oxidation experiments of Zn nanoparticles in air at 570K which showed that at this temperature they are completely transformed to ZnO retaining their original shape [15]. However, there are small differences in the O-K edge of the nanoparticles, as marked by the arrows. We believe that these differences may indicate the existence of native defects, such as Zn or O vacancies, in the
nanoparticles. Similar features in the O-K edge of the ZnO were interpreted by Sato et al. [16] as due to Zn vacancies when compared to theoretical calculations.

![Figure 5a. EELS spectrum of the O-K edge of ZnO nanoparticles and powder](image)

**Figure 5a.** EELS spectrum of the O-K edge of ZnO nanoparticles and powder.

![Figure 5b. EELS spectrum of the Zn-L edge of ZnO nanoparticles and powder.](image)

**Figure 5b.** EELS spectrum of the Zn-L edge of ZnO nanoparticles and powder.

4. **Conclusions**

ZnO quantum dots were grown on thermally oxidized (100) Si by evaporation of Zn metal in an MBE system and oxidation in oxygen flow. Characterization by TEM and EELS showed that the quantum dots were indeed ZnO single crystals grown with their c-axis perpendicular to the substrate and their distribution and size depends on the deposition parameters of Zn onto the substrates. This method of fabrication of ZnO quantum dots on SiO2 is compatible with Si based device fabrication processes and therefore can be used to incorporate ZnO quantum dots in such devices.

5. **Acknowledgements**

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6. **References**

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