



Photoemission study of ZnO nanocrystals: Thermal annealing in UHV and induced band bending

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ABSTRACT

ZnO nanocrystals distributed by spin-coating on SiO₂/Si surfaces were annealed in UHV and studied *in situ* by synchrotron radiation based X-ray Photoelectron Spectroscopy. Changes in chemical composition and electronic structure of ZnO nanocrystal surfaces were found with increasing annealing temperatures. Annealing at 650 °C reduces the surface contaminant levels without any observed de-composition of ZnO. After annealing at 700 °C an initial de-composition of ZnO together with further reduction of contaminants was observed. As a result, 650 °C is found to be the optimal annealing temperature for thermal cleaning of ZnO nanocrystals. Chemical changes and induced point defect formation cause changes in the band structure of the ZnO/SiO₂/Si system. An upward band bending of 0.7 eV on the surfaces of the ZnO nanocrystals was found after annealing at 300 °C. The bands on the surfaces of ZnO nanocrystals gradually bend downwards with increasing annealing temperatures. A downward band bending of 1.4 eV is the result after annealing at 750 °C for 1 h. This large downward band bending is explained as due to the change in balance of oxygen vacancies and zinc vacancies on the surfaces of ZnO nanocrystals.

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1. Introduction

The II–VI semiconductor ZnO in general and ZnO nanostructures in particular are currently receiving a large research interest. With a wide direct band gap of 3.4 eV and a large exciton binding energy of 60 meV [1], ZnO is a strong candidate for new optoelectronic applications such as photodiodes and solar cells [2–5], and light emitting devices [6–8]. Other reasons for the renewed interest are the possibilities to grow ZnO nanostructures in a wide variety of shapes with different properties [9]. For further reviews of ZnO properties see *e.g.* [10–14]. When ZnO nanocrystals (NCs) are used in a composite material, interactions with the other components occur through the surfaces so better known surface conditions are essential to obtain efficient applications. One important way to prepare well-defined surfaces is to clean and modify the surfaces through annealing. However, it is still not well known how thermal processing influences the surfaces of ZnO NCs, by *e.g.* desorbing contaminants and changing concentrations of point defects such as oxygen vacancies (V_O) and zinc vacancies (V_{Zn}) [15–17].

In our earlier study using SPELEEM [18], analyses of data from 10 μm μ-XPS spots showed that annealing at 650 °C cleaned the surfaces of ZnO NCs from hydroxide contaminants while yielding no sign of ZnO de-composition. In this report we have expanded the annealing temperature range to 750 °C and used synchrotron radiation based high resolution X-ray Photoelectron Spectroscopy (XPS)

to characterize annealing related changes of the surfaces of ZnO NCs. We note a strong thermal cleaning effect and a large temperature-dependent band bending related to changing point defect concentrations.

2. Experimental

Samples were prepared by spin-coating dispersions of ZnO NCs with an average size of 70 nm on SiO₂/Si substrates, prepared similarly to our previous study [18]. In order to obtain general results for ZnO NCs we have used NCs of mixed shapes, exhibiting different surface terminations, sparsely distributed on SiO₂/Si. The samples were annealed in UHV at 300 °C (1 h), 650 °C (1 h 45 min), 700 °C (1 h), and 750 °C (1 h) using direct current heating of the SiO₂/Si substrate. An infrared pyrometer was used to monitor the sample temperature.

XPS characterization was done at beamline I311 at the MAX-lab synchrotron radiation facility in Lund, Sweden [19]. The end station is equipped with a Scienta SES200 analyzer with an acceptance angle of 15°, enabling spectra resolutions of 22 meV at $h\nu = 140$ eV, 185 meV at $h\nu = 650$ eV and 775 meV at $h\nu = 1250$ eV with the used settings. All XPS data acquisitions were done at ambient temperature, collecting photoelectrons in the sample normal direction, after excitation with photon incident 55° from the sample normal. For high surface sensitivity the photon energies in high resolution spectra were chosen to obtain electron mean free paths of 1.0–1.4 nm [20,21], *i.e.* 3–5 atomic layers. High resolution XPS spectra were recorded for the Zn 2p_{3/2} ($h\nu = 1250$ eV), O 1s ($h\nu = 650$ eV), C 1s ($h\nu = 390$ eV), Si 2p ($h\nu = 140$ eV), and the Zn 3d/valence band

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($h\nu = 150$ eV) regions. The binding energies (E_B) in high resolution XPS spectra were referenced to the Fermi level (E_F) as measured from a Ta clip on the sample holder. All spectra were normalized with respect to the photon flux and a Shirley background was removed [22]. The fitting process was done by minimizing chi-square in a recursive process in the freely downloadable software FitXPS [23]. Using a linear background, Zn $2p_{3/2}$ spectra were fitted using a fixed Lorentzian line width of 0.8 eV and a varying Gaussian line width for the different components.

3. Results

To study the effect of different annealing temperatures on the surface chemical and electronic structure of ZnO NCs, XPS spectra were recorded. In Fig. 1(a) an XPS wide scan using $h\nu = 1350$ eV after annealing at 300 °C, with the E_B scale aligned to C 1s at 285.0 eV, is shown. Photoemission and Auger lines originating from ZnO, SiO₂/Si and C are found, but no other significant contributions. The insert in Fig. 1(a) shows a schematic image of the sample structure with individually separated ZnO NCs and agglomerates of ZnO NCs on the SiO₂/Si substrate.

As shown in the high resolution spectra in Fig. 1(b), the Zn $2p_{3/2}$ photoemission line shifts to a higher E_B with increasing annealing temperatures. The magnitude of these shifts, relative to the E_B observed after 300 °C annealing, are 0.7 eV (650 °C), 1.2 eV (700 °C) and 2.1 eV (750 °C)

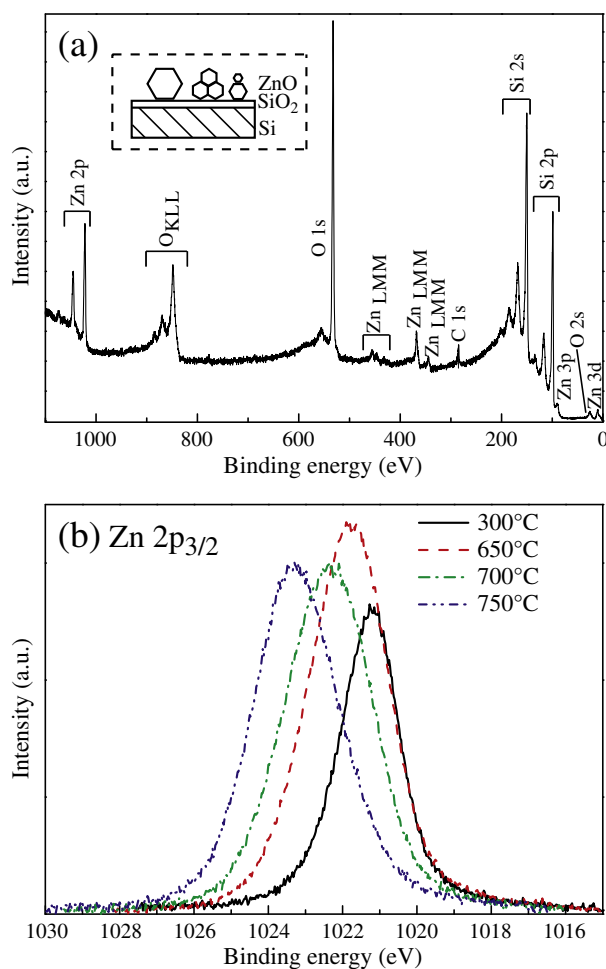


Fig. 1. (a) XPS wide scan from ZnO NCs on SiO₂/Si with peak designations acquired after annealing at 300 °C. The insert shows a schematic cross-section of the sample structure. (b) Zn $2p_{3/2}$ spectra after different annealing temperatures. Note the large shifts to higher E_B with increasing annealing temperature.

(750 °C), *i.e.* the total observed shift is more than 60% of the band gap of ZnO. We note that the Zn related Auger lines in the wide scans and the Zn 3d photoemission line studied using $h\nu = 150$ eV all shift with increasing annealing temperatures in a very similar way as Zn $2p_{3/2}$ (not shown).

From curve fitting of the Zn $2p_{3/2}$ spectrum the component from stoichiometric ZnO is noted to appear at an E_B of 1021.8 eV after annealing at 650 °C. This E_B and the difference between the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks, 23.15 eV, are in good agreement with the literature values for ZnO [24,25]. Fig. 2 shows the components in the curve fitted Zn $2p_{3/2}$ spectra after different annealing temperatures, plotted with the stoichiometric ZnO component at 0 eV. Details for the components are also shown in Table 1. The fitted spectrum after annealing at 300 °C, shown in Fig. 2(a), shows stoichiometric ZnO as the main component, a small component from Zn atoms in oxygen deficient regions of ZnO (V_O) on the low E_B side of ZnO [26], and a large contribution on the high E_B side. The component on the high E_B side originates from Zn bonded to contaminants, *e.g.* OH, H₂O and C [27–29], and Zn deficient regions (V_{Zn}). Since both these high E_B components appear at similar E_B they are difficult to de-convolute separately. We therefore denote these as “high E_B components” in Zn $2p_{3/2}$.

Increasing the annealing temperature from 300 °C to 650 °C causes a decrease in the contribution on the high E_B side, as shown in Fig. 2(b) and Table 1. The contribution from stoichiometric ZnO increases and shifts to 0.7 eV higher E_B while V_O on the low E_B side remain almost unchanged at a low intensity. Thus, annealing at 650 °C results in a reduction of contaminants on the ZnO surfaces, possibly together with a decrease of V_{Zn} , which is known to be reduced by annealing [1,30].

A further increase of the annealing temperature to 700 °C causes a decrease in intensity of the contribution from stoichiometric ZnO while the V_O intensity on the low E_B side increases, as shown in Fig. 2(c). Also on the high E_B side an increase is noted, interpreted as due to the creation of Zn deficient regions, V_{Zn} . Annealing at 700 °C is thus concluded to increase the density of both V_O and V_{Zn} , *i.e.* a de-composition of the ZnO NCs occurs. Interestingly, the stoichiometric ZnO component shifts a further 0.5 eV towards higher E_B , compared to the position after 650 °C annealing.

After annealing at 750 °C the component from stoichiometric ZnO in Zn $2p_{3/2}$ shifts 0.9 eV further towards higher E_B , yielding a total shift of 2.1 eV observed in this experiment. As shown in Fig. 2(d), the intensity of the stoichiometric ZnO component continues to decrease due to a further de-composition of ZnO. Accompanying this decrease both the V_O component and the high E_B components increase. The component from oxygen deficient regions, V_O , is also noted to broaden compared to that after 700 °C annealing. We assign this broadening as due to the creation of two different bonding configurations for zinc ions in the vicinity of V_O , with one and two broken bonds respectively, as proposed by Tay et al. [26]. A similar broadening effect is expected to happen in the high E_B components, through the creation of different numbers of missing zinc ions in the vicinity of the probed state. This would explain the difficulty in de-convoluting the spectra into two components.

The asymmetry on the high E_B side of the C 1s peak in Fig. 3(a), recorded after 300 °C, clearly shows the presence of two components. Annealing at 650 °C almost completely removes a smaller component at around 286 eV, assigned to CO compounds [31], and decreases the remaining component at around 285 eV to below 60%. This overall intensity decrease in C 1s coincides with the large increase in Zn $2p_{3/2}$ intensity from 300 °C annealing temperature to 650 °C. The intensity for the remaining component at 285 eV, assigned to CC and CH compounds [31], decreases to its lowest intensity, although still clearly present, after 700 °C annealing. However, after annealing at 750 °C the C 1s intensity increases again. We assign this increase as due to carbon migration to the surface of the SiO₂/Si substrate, since

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