Supporting information for manuscript “Influence of ZnO nanowire array morphology on field emission characteristics” by S, Garry *et al.*

Sample preparation

ZnO buffer layer

Silicon substrates with (100) orientation were coated with a ZnO buffer layer in order to initiate ZnO nanowire growth and to ensure c-axis alignment. No attempt was made to remove the substrate native oxide layer in any case. Firstly a ZnO seed layer is deposited by drop coating a 5 mM solution of zinc acetate in absolute ethanol [1]. 3.5 µl of this solution is applied per cm^{-1} of substrate area. After 20 seconds the substrate is rinsed with absolute ethanol and dried with a nitrogen stream. This process is repeated 5 times, after which the substrate is annealed at 350°C for 30 minutes to produce a thin ZnO seed layer. This layer is then used to initiate CBD growth of a thicker ZnO layer. The seed layers are submerged in a 25 mM zinc acetate solution in DI-H_2O at 60 - 70°C for 3 hours. In order to reduce incorporation of precipitates onto the substrates after 90 minutes, they are removed from the solution and rinsed with DI-H_2O and then submerged in a fresh zinc acetate solution for a further 90 minutes. After deposition the substrates are cleaned by sonication in fresh DI-H_2O and dried with a nitrogen stream [2].

Silica mask

The ZnO buffer layers were first coated with a monolayer of close-packed polystyrene nanospheres using the technique proposed by Rybczynksi *et al*. [3] whereby a nanosphere monolayer is suspended at the air-water interface of DI-H_2O in a Petri dish. Nanosphere monolayers are deposited by submerging the substrate in the DI-H_2O and slowly withdrawing the substrate through the nanosphere layer. The coated substrate is then allowed to dry in air before annealing at 110°C for 40 seconds in order to improve nanosphere adhesion as it is essential that the nanospheres make good contact with the ZnO buffer layer [4]. A silica sol is then prepared by mixing 1 ml of TEOS with 1 ml of 0.1 mM HCl in 20 ml of absolute ethanol [4]. The solution is stirred for three hours and immediately prior to use diluted with an equal volume of ethanol. 20 ml of this sol is drop coated on each sample, which was agitated slightly during drying in order to evenly distribute the sol. After a short period of drying, the substrate is placed on its edge in order to allow any excess sol to run off. The substrates are then dried for 10 minutes by heating at 90°C. The polystyrene nanospheres are then removed by dissolution in toluene followed by acetone. Finally the silica layer is densified by heating at 550°C using a ramp rate of 15°C per minute [4].

Nanowire deposition

ZnO nanowires were deposited using two techniques, CBD and VPT. For CBD depositions substrates coated with a patterned silica mask are submerged in a 25 mM zinc acetate solution in DI-H_2O for 90 minutes at a temperature of 60 - 70°C. After deposition the substrates are rinsed in DI-H_2O and dried under a stream of nitrogen.

Samples deposited using VPT first have a short nanowire growth sequence by CBD using the technique outlined above for 30 minutes. After the CBD step the substrate is rinsed in DI-H_2O and dried as before. Equal masses of graphite and ZnO (60 mg) are thoroughly mixed using a pestle and mortar and transferred to an alumina boat. The substrate is placed ~1 cm above the mixture with the prepared and templated side facing the source materials. The boat was heated at 800°C for 10 minutes and then ramped to 900°C at a rate of 10°C per minute. Deposition is carried out at the centre of a single zone tube furnace with a 90 sccm flow of argon. The total growth time is 1 hour after which the furnace is allowed to cool to room temperature. Further details of the growth system are given in references [5, 6].

Since CBD deposition occurs on all areas of the substrate not masked by the silica template, the diameter of nanowire deposited in this way is determined by the size of the apertures. This effect, combined with the tendency of Zn acetate derived CBD nanowires to be wider at the tip than at the base, due to the capping effect of the zinc acetate ions in the solution, places a limit on the length of nanowires which may be grown in this way as they will eventually coalesce into thin films. The result of these effects is that CBD nanowires produced here are generally much shorter and wider than VPT nanowires; however CBD nanowire arrays exhibit excellent uniformity, in terms of both nanowire diameter and length, compared to the more random nanowire morphologies produced using VPT. Nanowire length may be controlled reliably by altering the growth time, as the growth rate remains steady over time.

Changes in nanowire morphology and damage following FE

Changes in morphology occurred during FE which may be broken down into two broad categories; melting, likely due to Joule heating in each nanowire during emission, and a significant structural disruption of the substrate such that ZnO nanowires, buffer layer, and Si substrate apparently violently ‘exploded’ over the surrounding area.

In most cases melting was confined to the tips of individual nanowires as shown in figure 1. Melting of this nature has been reported by Semet *et al.* and it attributed to a surface diffusion process caused by the high temperatures during FE [7]; that report deduces that the temperatures occurring during emission may be > 1600K.

However, more extreme melting was also observed, with whole nanowires being vaporised. This type of damage was also observed on most samples examined but was not widespread, and accounted for only a small portion of total sample area in all cases; an example of this damage is shown in figure 2. While the effect of this kind of damage on FE is not fully understood it is assumed that it does not significantly alter FE performance or subsequent analysis since it covers relatively small areas of each sample.

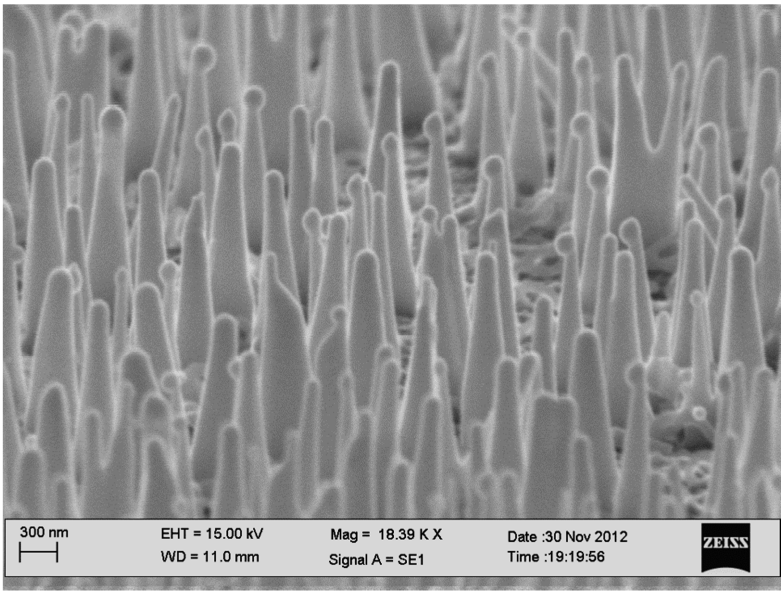

Figure 1: Example of nanowire melting prevalent over large areas of samples examined post-FE.

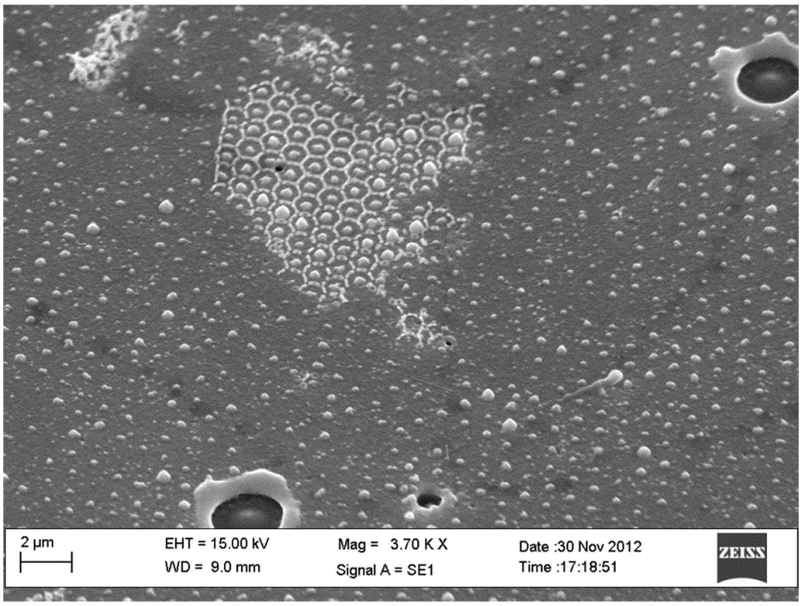

Figure 2:Example of area where all nanowires have vaporised, this damage was localised and represents only a small fraction of total sample area.

Figures 3 shows examples of the catastrophic ‘explosive’ damage exhibited by a number of samples post-FE; all the ZnO nanowires and the buffer layer have been entirely removed and the underlying Si substrate shows signs of melting and catastrophic damage. This kind of damage tended to occur in clusters, believed to be caused by arcing during sample conditioning. The conical structures observed at these points of disruption are Si material (based on energy dispersive x-ray measurements in the SEM system) which has been melted due to the high current density during an arcing event. This type of disruption was described by Spindt *et al.* [8] as a runaway gasification event. These disruptions are likely to have significant impact on the nature of the I-V data gathered from those samples exhibiting this damage because the tips of the conical Si structures are in some cases several µm higher than the surrounding ZnO nanowires. It is likely that following their formation, significant emission occurs from these points causing reduced emission from the surrounding ZnO nanowires due to the screening effect. Additionally, since these conical structures consist of Si and not ZnO, any FN analysis carried out on their I-V data may lead to incorrect values for the field enhancement factor since this analysis is critically dependent on the work function used. For these reasons, the I-V data gathered from these samples are considered unreliable and not considered for further FE analysis. All three CBD samples examined, along with two VPT samples, were damaged in this way.

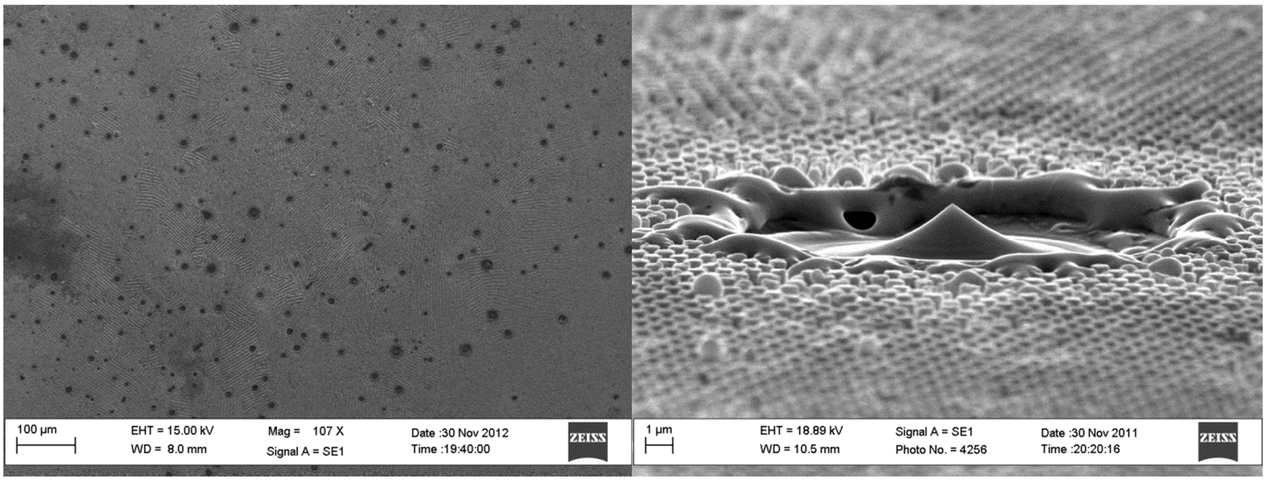

Figure 3: SEM images of areas exhibiting arcing damage. The left image is an example of a cluster of such areas while on the right is an image taken at a 80° tilt in order to show conical Si structure.

References for supporting information

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