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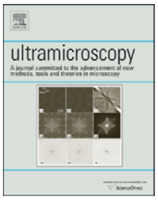

Growth and field emission properties of ZnO nanostructures deposited by a novel pulsed laser ablation source on silicon substrates

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ABSTRACT

Zinc oxide (ZnO) nanostructures were produced using a novel pulsed laser ablation apparatus comprising in-situ analysis of the plume by reflection time-of-flight mass spectrometry. Various morphologies of nano and microstructures were obtained for laser wavelengths of 1064 and 355 nm, and oxygen ambient pressures of 10^{-6} and 10^{-2} mbar, respectively. None of the produced structures exhibited a particular type of self-organisation whereas all of them showed low aspect ratios and good field emission properties. Optimum values of 5.2 V μm^{-1} and 2060 were obtained for the turn-on field and Fowler–Nordheim enhancement factor, respectively, for deposited nano-tipped microstructures presenting a high coverage of the substrate. The experimental data showed that for a given laser wavelength, higher field enhancement factors were obtained for the samples grown at the lower pressure of 10^{-6} mbar. In these conditions, the deposited materials showed distinct nanostructuring and comparison with existing data showed the corresponding ablation plumes to contain $(ZnO)_n$ clusters, up to $n = 13$. This work also shows that the electronic properties of the nanostructured ZnO produced in our conditions, as determined by the oxygen concentration during deposition, have an influence on the field emission properties in addition to the nanostructure morphology.

1. Introduction

There is currently an interest in the development of new field emission (FE) electron sources (cold cathodes) for use in future technologies such as miniature X-ray sources [1] or novel flat panel displays [2]. This has been driven by the relative failure of carbon nanotubes to reach the initially hoped for role as the ultimate cold cathode in spite of intensive research in the past decade [3,4].

Materials that readily form wire-like structures and have attractive electronic and material properties such as a low work function and high thermal stability are the obvious alternatives as they should form efficient and stable electron sources. One such material is the n-type semiconductor ZnO which has a direct wide band gap of 3.3 eV and is therefore a natural candidate for a surface with low electron affinity and work function, respectively. Furthermore, a substantial body of work has demonstrated in the past few years that ZnO is one of the most versatile materials for the fabrication of a plethora of nanostuctures, including nanorods and nanowires [5]. Thus, the FE properties of ZnO nanowires/nanopins were recognised some years ago [6] and continue to generate a considerable research effort (e.g. [7–9]).

Recent works on the enhancement of FE in nanostructured ZnO (nZnO) have also concentrated on the optimisation of its structural and electronic properties. Specific growth and fabrication methods have been developed by various authors to control and optimise the shape (sharp tip) and aspect ratio (height to width) of the nZnO emitters [10–12]. The optimisation of the electronic properties of field emitters by various surface treatments such as oxygen anneals, plasma treatments or ultra thin film deposition have also been investigated [13,14].

Pulsed laser deposition (PLD) has recently been recognised as a suitable technique for the production of FE device-quality ZnO nanowires/nanorods with the corresponding growth mechanisms debated by the authors [15–17]. Here we have developed a novel laser ablation source in which the plume expands along a direction parallel to the substrate surface for deposition, thus allowing for simultaneous mass analysis with the help of an in-situ reflectron time-of-flight (ReTOF) mass spectrometer. We have studied the conditions in which optimised field emitters are produced and their possible relationship to both the processes of plume cluster formation and nZnO growth. We present the first results obtained with this new apparatus in the following sections of the paper.

2. Experimental details

Samples were grown using PLD, in a custom-designed system schematically represented in Fig. 1. A Q-switched Nd:YAG laser was used either at the fundamental wavelength of 1064 nm or the wavelength of 355 nm after frequency-tripling. The pulse width was about 6 ns for both wavelengths and the pulse repetition rate

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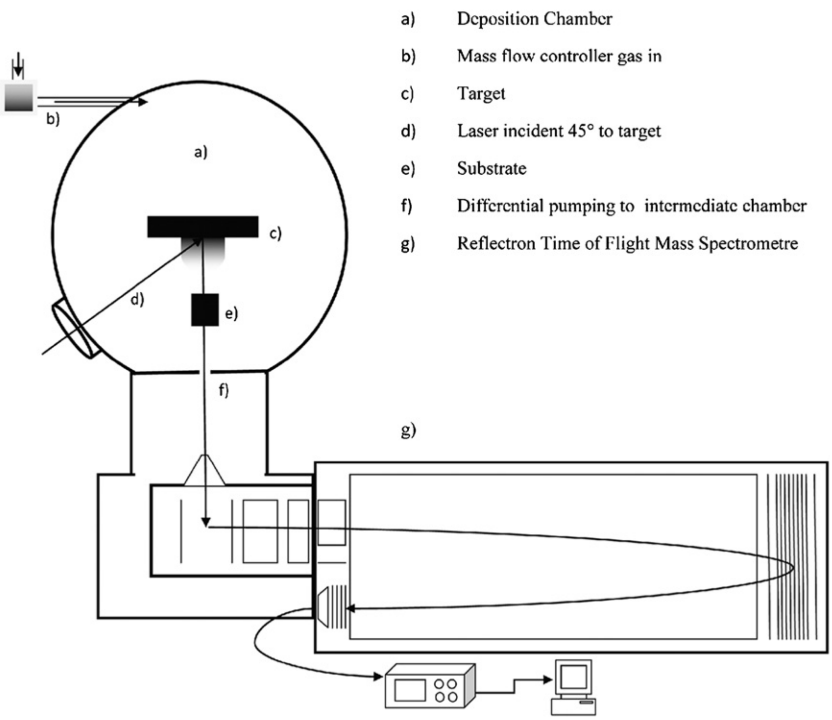

Fig. 1. Schematic representation of the PLD system with in-situ ReTOF mass spectrometer.

was 10 Hz. The fluence on target was kept fixed at ~7.7 J cm^{-2} and obtained with a focal spot diameter of ~1 mm at 45° incidence. The target was a 5 N purity ZnO ceramic disk, which was continuously rotated and translated during deposition so as to present a fresh surface for each laser shot. The depositions were carried out either in a high vacuum at a pressure of 10^{-6} mbar or in an oxygen ambient pressure of 10^{-2} mbar using a mass flow controller at a rate of 30 sccm. The depositions were performed at room temperature on phosphorus-doped n-type Si (111) substrates placed parallel to the expansion of the plume, 5–7 cm away from the target (see Fig. 1). Substrates were degreased using an ultrasonic cleaning procedure prior to growth. Nine thousand laser shots were used for each deposition.

The FE properties of the deposited materials were obtained from their *I–V* characteristics. The latter were measured in a vacuum chamber (base pressure 10^{-7} mbar) using an anode made of a flat polished aluminium plate mounted on a translation stage. The assembly of the ZnO layer deposited on the conducting silicon substrate constituted the counter-electrode (cathode) and was positioned on a polytetrafluoroethylene (PTFE) block with an electrical feedthrough in its centre connected to the back of the substrate via conductive paste. A PTFE spacer of 100 μm thickness with a circular hole of diameter 2.5 mm in its centre was used to control the anode–cathode separation distance. The *I–V* characteristics were recorded using a computer controlled data acquisition system interfaced via GPIB to a SRS PS350 high voltage source (*V*) with a current feedback loop through a Keithley 6485 picoammeter (I).

The morphology of the grown materials were characterised by scanning electron microscopy (SEM).

3. Results and discussion

The sample morphologies are presented in Fig. 2. The laser wavelength and growth pressures corresponding to samples of Fig. 2(a), (b), (c) and (d), hereafter referred to as samples (a), (b), (c) and (d), were 1064 nm at 10^{-2} mbar of oxygen, 1064 nm at 10^{-6} mbar, 355 nm at 10^{-2} mbar of oxygen and 355 nm at 10^{-6} mbar, respectively. All other experimental conditions were kept constant and described previously in Section 2.

In the conditions of Fig. 2(a) long narrow microstructures are obtained, randomly distributed over the surface, with typical length of ~10 μm, no other structures are seen at greater magnifications. In Fig. 2(b) both long (10–15 μm), narrow (0.2–0.5 μm) microstructures and nano-particles (150 nm) are observed. Both structures appear to be randomly distributed across the surface. The magnification in this case has been optimised to show more clearly the two types of structure. In the conditions of Fig. 2(c), one observes oblong nanostructures with average widths of 170 nm, average lengths of 350 nm while the average inter-structure spacing is typically 1 μm. Finally, in Fig. 2(d) we observe some self-organised growth of microstructures with dense packing on the surface and consistent heights and widths of ~1 and 0.5 μm, respectively.

The detailed in-situ ReTOF plasma diagnostics of the ablation plumes corresponding to the growth conditions of samples (a)–(d) have been reported elsewhere [18] and the reader is referred to this reference for more-detailed information about the corresponding mass spectra. We summarise here only the results relevant to the present study. For sample (a) no mass spectra for $(ZnO)_x$ clusters could be detected whereas the ablation plume of sample (b) showed mass spectra corresponding to Zn and ZnO with their dimers and cluster groups containing 6 zinc atoms and oxygen atoms varying between $x = 6$ and 9. The plume corresponding to sample (c) gave mass spectra showing the presence of Zn_x and $(ZnO)_x$ with $x = 1$ and 2 only. Finally, mass spectra of the plume for deposition of sample (d) was rich in Zn_x and $(ZnO)_x$ clusters with x up to 13. Energy dispersive X-ray spectroscopy (EDX) was also performed on all samples and indicating the presence of Zn and O peaks for all the samples.

The *I–V* curves of samples (a)–(d) and their FE properties obtained from Fowler–Nordheim (FN) plots are shown in Figs. 3(a) and (b), respectively. The turn-on field is determined