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Fabrication and field emission performance of arrays of vacuum microdiodes containing CuO nanowire emitters grown directly on glass without a catalyst

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Arrays of vacuum microelectronic sources are fabricated on a glass substrate using cupric oxide (CuO) nanowire emitters. The arrays of electron sources possess a microdiode structure, which can effectively induce field emission and control the delivery of emitted electrons to the anode in a triode-type device operation. A technique for precisely growing CuO nanowires at the centre of microcavities in an array without using a catalyst and at temperatures as low as 400°C is presented. Such a simplified fabrication procedure results in improved field emission performance from the array compared with previous vacuum microelectronic devices. Typical prototype devices have turn-on gate voltages as low as 169 V to give emission current densities of 10 μA/cm^2 at the anode. The ratio of anode current to cathode current reaches ~0.85, and the maximum change in emission current density per volt is 1 μA/cm^2. Electron emission from the arrays is stable and reproducible under either pulsed or direct current fields. These characteristics indicate that microgate-controlled CuO nanowire emitters may find application in practical devices.

field emission, CuO nanowires, vacuum microdiodes arrays, emitters

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Carbon nanotubes (CNTs) and various nanowires have been shown to possess attractive field emission properties and have been investigated for potential application as electron emitters in vacuum devices [1–3]. In applications such as miniaturized microwave devices [4], mass spectrometers [5, 6], parallel electron beam lithography [7], and large-panel field emission displays (FEDs) [8–10], the vacuum electron sources need to be controlled by microgates to minimize the driving voltage provided by the integrated circuit chip. To achieve this goal, vacuum microdiodes structures have been developed and the Spindt-type microcavity structure is often adapted [11–28]. To make use of efficient field electron emission nanomaterials such as carbon nanotubes and nanowires as nanoemitters, various microfabrication techniques have been developed taking into account of the effects of the self-assembly processes of nanotubes and nanowires. The central issue is to control the position, height, alignment, packing density and uniformity of nanoemitters within microcavities in the FED. Much effort has been devoted to resolve the complications induced in growing nanoemitters brought about by necessity of a depositing catalyst. Most of the reported studies on microdiodes use carbon nanotubes/fibers and only a few have used nanowires. Lee et al. [21] demonstrated a successful example where a catalyst layer was deposited on a substrate through a hole opened inside the microcavity, which allowed subsequent growth of a group of CNTs. Gangloff et al. [22] used a similar procedure but were able to grow a single carbon nanotube in each microcavity by reducing the number of catalyst particles to one. Lee et al. [23] also employed similar method to fabricate a microdiode containing a group of ZnO nanowire emitters. The difficulty with the

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direct deposition of catalyst is avoiding contamination of the inside of the microcavity. To overcome this difficulty, Guillorn et al. [24] grew a single CNT array first and then made a microcavity, which used a CNT as its central axis. Recently, Jiaojun et al. [25] reported a new method combining the advantages of the above two methods. The catalyst layer was buried under multiple layers and was then exposed by ion beam milling using a dual beam focused ion beam system. Using this technique, the milling procedure needs to be carefully controlled and efficient activation of catalyst particles is required.

In this work, a new method that does not require the use of a catalyst is reported; CuO nanowire emitters are grown at the centre of a microcavity by thermal oxidation of a thin film of Cu in air. This method has multiple advantages, including: (i) no need for catalyst deposition, (ii) simple experimental setup for thermal oxidation, and (iii) thermal oxidation proceeds at 400°C so a glass substrate can be used. As a result, this method is simple and applicable to the preparation of large area vacuum microelectronic source arrays.

1 Fabrication process

A schematic diagram of the fabrication process used to make the vacuum microdiode is illustrated in Figure 1. The technical procedure for the preparation of vacuum microelectronic arrays using CuO nanowire emitters is as follows. Films of buffered chrome (Cr, 50 nm thick), copper (Cu, 0.9 μm thick) and aluminum (Al, 2.5 μm thick) were sequentially deposited onto a glass substrate by DC magnetron sputtering, as shown in Figure 1(a). This was followed by plasma-enhanced chemical vapor deposition of silicon dioxide (1.2 μm thick) and silicon nitride (0.4 μm thick) films, respectively. The buffered layer of Cr between the glass substrate and the Cu layer assures that the Cu film remains adhered to the glass substrate. A Cr gate electrode with a thickness of 0.5 μm containing an array of cathode holes with diameters of 40 μm is prepared by a lift-off process, as shown in Figure 1(b). Using this patterned Cr film as a mask, insulating layers of Si_3N_4 and SiO_2 are then etched by a dry reactive ion etching process (Figure 1(c)). Because the etching rate of Si_3N_4 is larger than that of SiO_2, a groove forms in the Si_3N_4 layer, which effectively prevents electrical breakdown between the cathode and gate electrodes. To fabricate a smaller hole to expose the Cu surface in the center of the existing larger hole, a second process involving photolithography and wet etching of Al was performed, as shown in Figure 1(d). Finally, CuO nanowires were grown in a self-assembly process by thermal oxidation of the Cu thin film at 400°C for 3 h in air.

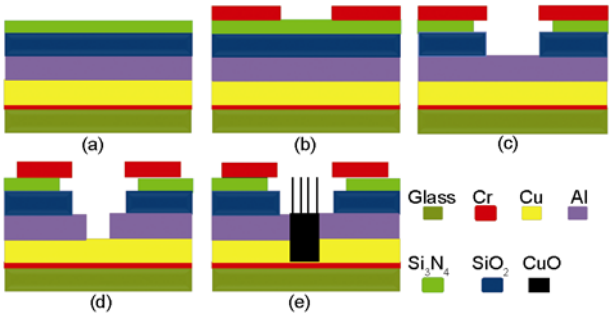

Figure 1 Schematic description of the fabrication process of a vacuum microdiode using CuO nanowire emitters self-assembled in a gate-controlled microcavity.

2 Results and discussion

Scanning electron microscopy (SEM) images of a typical device are shown in Figure 2. Each sample consists of 16 electrodes, each of which contains 16 pixels of microdiodes. Figure 2(a) shows the sections of three electrodes, each containing four pixels of vacuum microdiodes. Each pixel has 5×8 vacuum microdiodes (Figure 2(b)). The diameters of the gate-hole aperture and its inner hole are ~40 and ~20 μm, respectively (Figure 2(c)). CuO nanowires only grew within the inner hole, and thus the cathode area (A_0) of each pixel is about 1.27×10^{-4} cm^2. The current density is given by $J=I/(nA_0)$, where n and I are the number of pixels involved in emission and the total current measured, respectively. The CuO nanowires grown in each microdiode have diameters in the range of 30–80 nm and lengths in the range of 0.5–3 μm. The field emission of the device was characterized in a chamber under a base vacuum of 2.4×10^{-6} Pa.

To investigate the emission from a sample, green phosphor (ZnS)-coated indium tin oxide glass kept at a distance of 250 μm from the sample surface, was used as an anode. Figure 3 shows the typical changes in the field emission of 16 pixels on a single electrode in response to different gate voltages, which were recorded using a CCD video camera at a DC anode voltage of 1800 V. Video sequences showing the response of the pixels under pulsed fields were also recorded (see Supporting Information). In these devices, the gate voltage is responsible for inducing and controlling the field emission from the nanoemitters; some studies have used the gate voltage only to modulate the field emission that is induced across the hole by applying a high voltage to the anode. Obviously, not all of the pixels worked and the emission was not uniform; however, efforts are underway to overcome this problem. Figure 3 shows that a gate voltage of 40 V induces emission from one pixel to give a visible spot. As the gate voltage increases, the brightness and number of visible spots increase. At a gate voltage of 180 V, 9 out of the 16 pixels on this particular electrode produce visible spots.

Figure 4(a) shows that the currents collected by the anode are effectively controlled by the gate voltage V_g, and

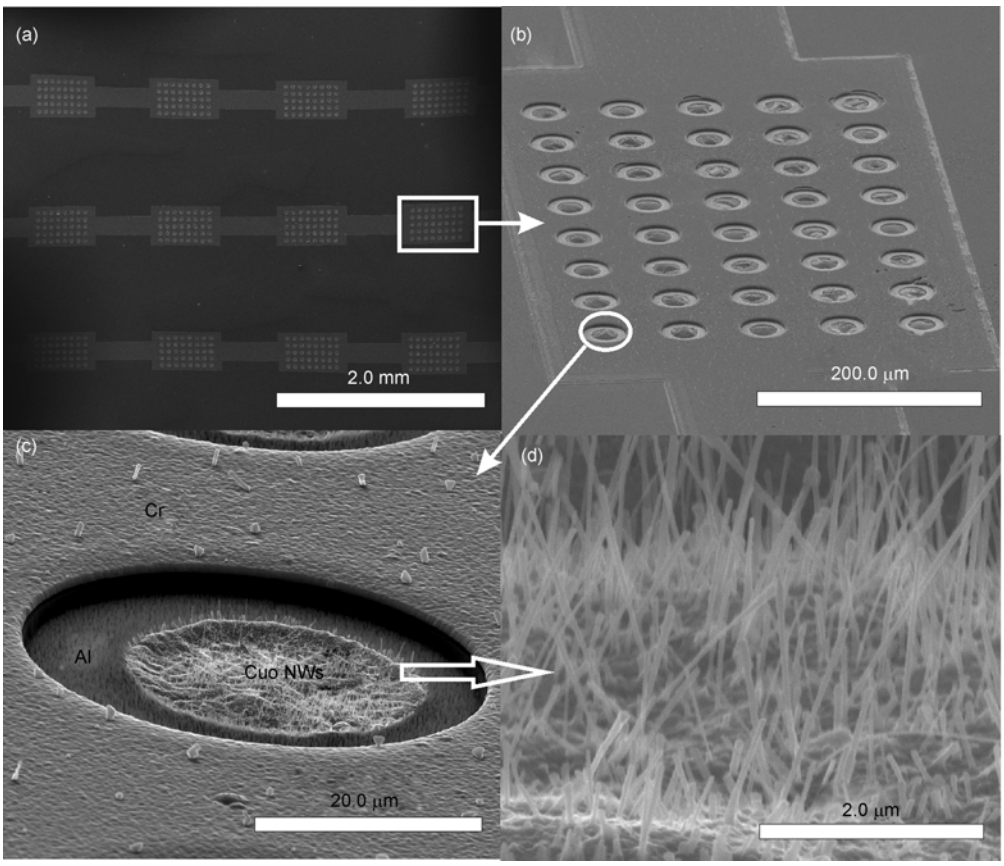

Figure 2 SEM images of microdiodes with CuO nanowire emitters. (a) Arrays of pixels (top view). (b) array of microdiodes in a pixel. (c) cross-sectional view of a microdiode. (d) CuO nanowires grown in the central hole of a microdiode.

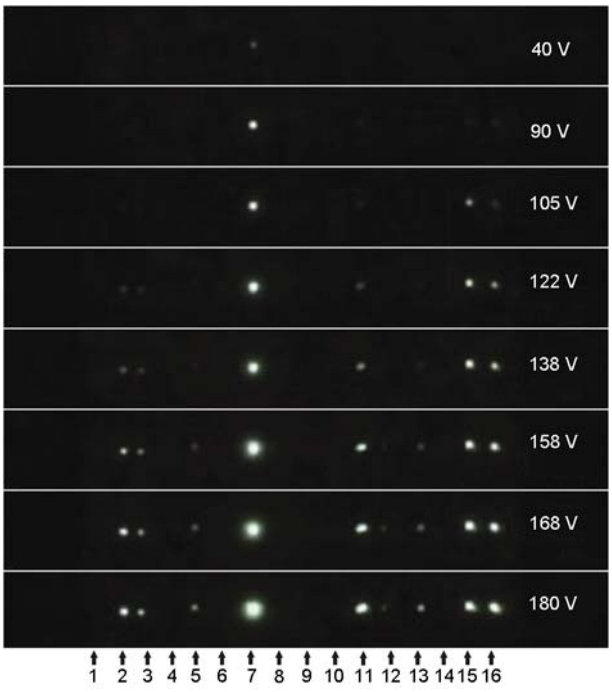

Figure 3 Images showing the changes in field emission in response to varying the gate voltage of the 16 pixels in one electrode at a DC anode voltage of 1800 V. The arrows and numbers at the bottom of the images indicate the position of the pixels in the electrode.

Figure 4(b) shows that the trends of anode current *versus* V_g follow Fowler-Nordheim (FN) behavior, which confirms that the anode current is induced by the action of V_g. In addition, both the anode current density J_a-V_g plot and corresponding FN plot are strongly affected by the anode voltage. The anode current increases the anode voltage V_a increases. Figure 4(b) also shows that the slope of the FN plots gradually decreases as the V_a increases. This is attributed to the collection of an increasing amount of emitted electrons. Finally, the turn-on gate voltage, which is defined as the gate voltage at which J_a reaches 10 μA/cm^2, decreases from 176 to 169 V because of the increase of V_a from 1200 to 1400 V. Voltages of this magnitude could be provided using commercial driving chips with high voltage outputs.

A vacuum microdiode using a gated microcavity presents two important issues: (i) leakage of current between the gate and cathode electrodes, and (ii) the efficiency of transmission of emitted electrons through the hole in the microgate to the anode. To clarify the issues, the relationship of the cathode current density J_c *versus* V_g was determined for various V_a (Figure 5(a)). The corresponding FN plots exhibit strong nonlinearity at low V_g (<~80 V) (Figure 5(b)). This is because leakage current is dominant and field emission is barely present. To see if this leakage current is significant and how effective the vacuum microdiode is at

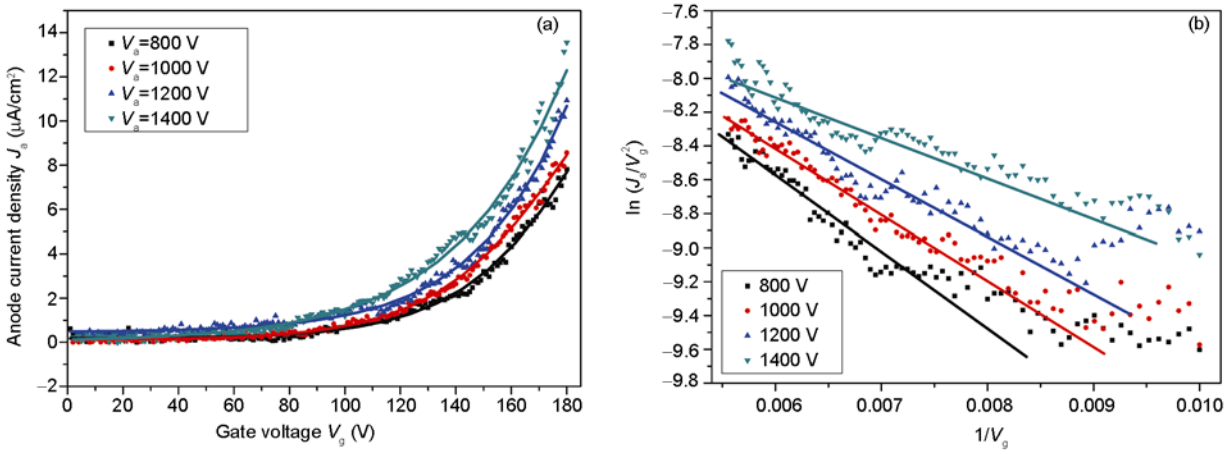

Figure 4 (a) Plots of anode current density J_a as a function of gate voltage V_g at various anode voltages V_a; (b) the corresponding F-N plots for different anode voltages.

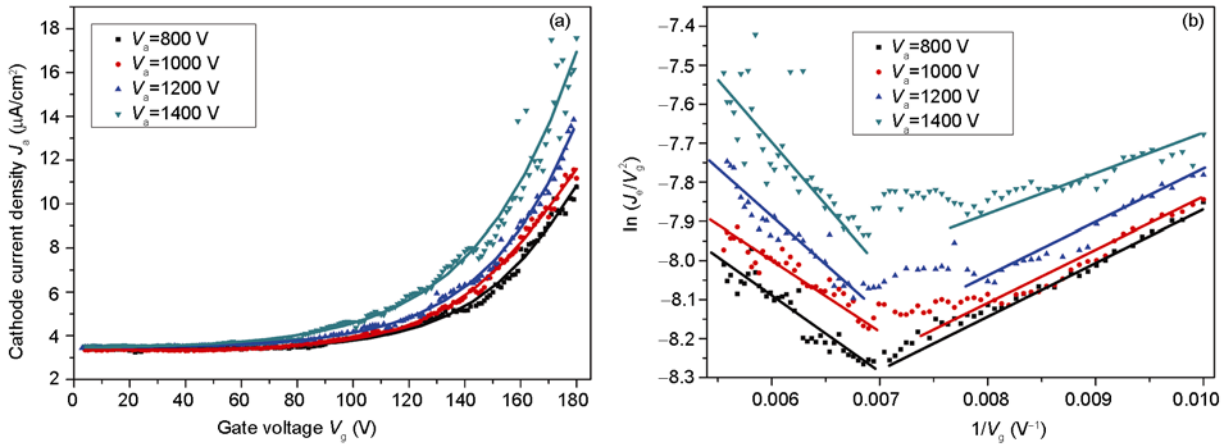

Figure 5 (a) Plots of cathode current density J_c as a function of gate voltage V_g at different anode voltages V_a; (b) the corresponding F-N plots.

inducing and transmitting emitted electrons, the ratio between J_a and J_c (i.e. J_a/J_c) was determined and plotted as J_a/J_c *versus* V_g at different V_a (Figure 6). The ratio of J_a/J_c increases with increasing V_g and V_a, reaching a maximum of ~0.85. This reveals that the devices developed herein operate effectively.

To understand the effect of increasing V_a on enhancing the efficiency of the current collected by the anode, an electron optical simulation was performed. Figure 7(a) shows that all of the electrons emitted in the axial direction from CuO nanowire emitters that are aligned vertically to the cathode surface (inset of Figure 7(a)) will affect the anode because of a focusing effect. However, the electrons emitted in the axial direction from CuO nanowire emitters that are not vertically aligned will not always be directed towards the anode by the electric field; instead some will affect the gate electrode. Upon increasing V_a, an increasing large portion of the electrons are steered towards the anode, as may be seen by comparing Figures 7(b) to (e).

The results from the relevant studies of vacuum microelectronic devices using nanoemitters reported previously are compared with the results of the devices developed here in Table 1. Table 1 shows that more detailed device charac-

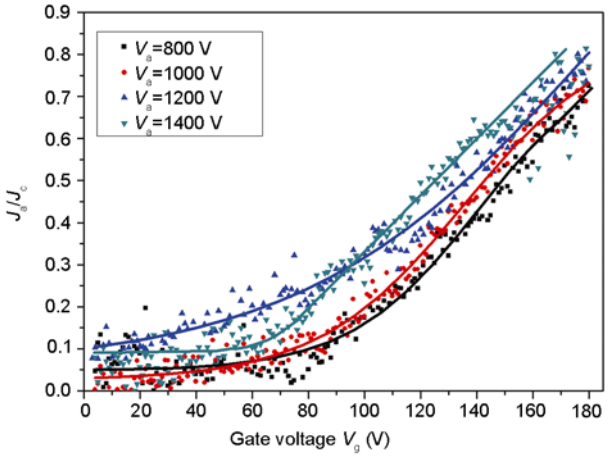

Figure 6 Plots of the ratio between anode current density and cathode current density J_a/J_c versus gate voltage V_g at different anode voltages V_a.

terization has been performed for the present prototype devices than in previous studies; this enables further evaluation of the potential of vacuum microelectronic devices containing nanoemitters. The following important features of the developed prototype devices are also apparent from Table 1: (i) low temperature growth of the nanoemitters, (ii) no catalyst is required, and (iii) use of a glass substrate.

Compared with typical results reported for other emitters grown in gate-controlled microstructures (Table 1), the developed FED containing CuO nanowire cathode emitters

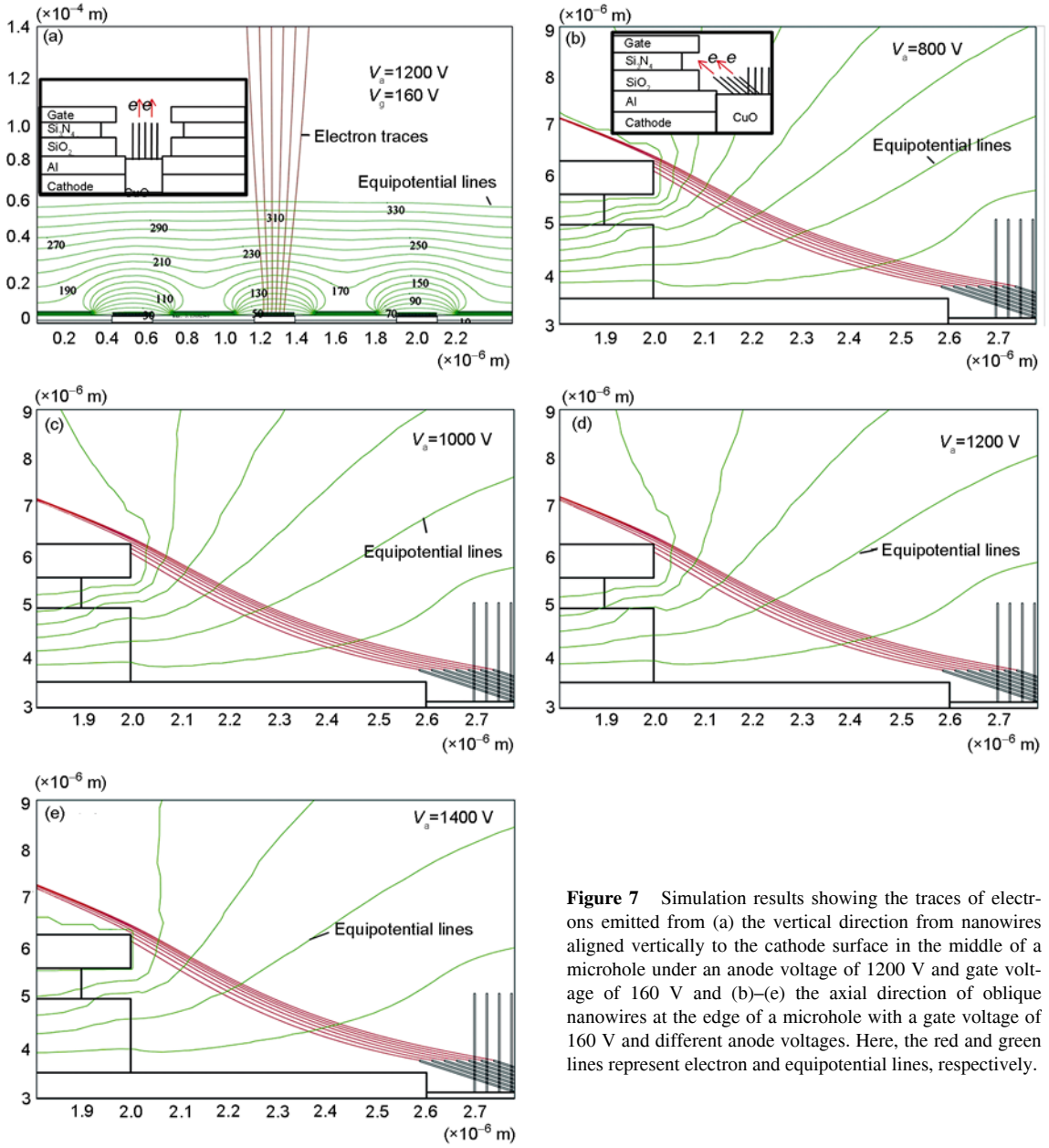

Figure 7 Simulation results showing the traces of electrons emitted from (a) the vertical direction from nanowires aligned vertically to the cathode surface in the middle of a microhole under an anode voltage of 1200 V and gate voltage of 160 V and (b)–(e) the axial direction of oblique nanowires at the edge of a microhole with a gate voltage of 160 V and different anode voltages. Here, the red and green lines represent electron and equipotential lines, respectively.

Table 1 Comparison of parameters for reported vacuum microelectronic devices

Type of emitters	Temperature of growth	Type of substrate	Catalyst	Test area of field emission
CuO [present study]	400°C	glass	no need	arrays
CNT &Si NWs [22]	675 & 800°C	Si	Ni/Au	array
CNT [25]	700°C	Si	Ni	array
ZnO [23]	900°C	Si	Au	not reported
CNP [26]	680°C	Si	Ni	not reported
CNT [27]	not reported	Si	Ni	single microcavity

grown inside a gate-controlled microstructure have great potential for practical application as electron sources. This is because of advantages such as good emission properties and the feasibility of fabricating devices with large areas at low temperature on glass substrates.

3 Conclusions

In summary, it was demonstrated that vacuum microelectronic devices containing arrays of nanoemitters as electron sources can be fabricated on a glass substrate at low temperature without using a catalyst. In particular, CuO nanowires can be grown directly from a Cu thin film exposed at the centre of a microcavity. Using a microcavity that is smaller than the gate hole, the growth of nanowires is limited to the central area of the microcavity, minimizing their contact with the gate electrode. The resulting prototype devices displayed attractive field emission performance. Gate voltages as low as 100 V can initiate field emission. The ratio of anode current to cathode current can reach ~0.85, and the maximum change in emission current density per volt was 1 $\mu A/cm^2$. The emitted electrons may be focused on the phosphor screen, and the resulting emission was stable and reproducible under either pulsed or direct current fields. These characteristics indicate that micro-gate-controlled CuO nanowire emitters may have potential in practical device applications.

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