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Field-emission properties of TiO_2 nanowire arrays

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Abstract
Aligned TiO_2 nanowire arrays were fabricated onto Si wafers by a simple thermal deposition (PVD) method. Scanning electron microscopy and high-resolution transmission electron microscopy observations confirm that the as-prepared TiO_2 nanowires are single-crystalline and of high purity. Field emission measurements showed that the TiO_2 nanowire arrays could provide stable, high-current electron emission at a low voltage. The emission current monitored over a period of 24 h fluctuated gently but did not show degradation. The cathode-luminescence (CL) images captured by a CCD camera were very bright and their CL intensity was homogeneous. This remarkable performance reveals that TiO_2 nanowire arrays are well suited for commercial use in electron devices, particularly flat panel displays.

1. Introduction

In recent years, vertically-organized one-dimensional nanostructure-based field emitters (e.g. nanowire and nanotube arrays) have attracted great interest owing to their potential applications in flat panel displays and vacuum microelectronics [1–7]. Field emission properties of carbon nanotubes (CNTs) have been widely investigated [8–12]. Wide band-gap semiconductors have also stimulated considerable attraction as promising cold-cathode materials because of their low electron affinity and chemical stability. It has been reported that needle-shaped silicon carbide nanowires are suitable for field electron emission [1]. Zhou *et al* [2] also reported that the emission current from aligned MoO_3 nanowires is relatively uniform and stable. The field emission from ZnO nanostructured materials was also studied by some research groups [3–6]. Some techniques have been developed for preparing TiO_2 nanowires or nanotubes. TiO_2 nanowires were successfully fabricated into nanochannels of porous templates by Caruso *et al* [13]. Zhang *et al* [14] also reported the synthesis of TiO_2 nanowires by a chemical synthesis method. Moreover, Lei *et al* [15] successfully obtained TiO_2 nanowire arrays through a sol–gel method. However, these wet-chemical methods cause contamination in the products. Furthermore, the above-mentioned methods are difficult to integrate with conventional microfabrication process. In this paper, we report the field emission behaviour of high quality,

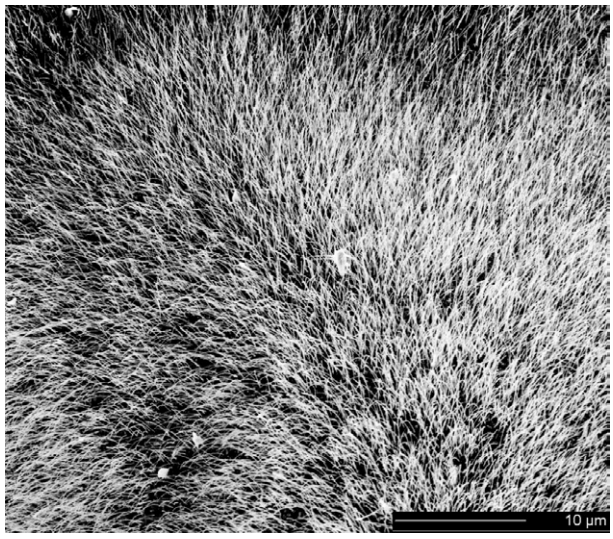

Figure 1. SEM image presenting the morphology of the nanowire arrays.

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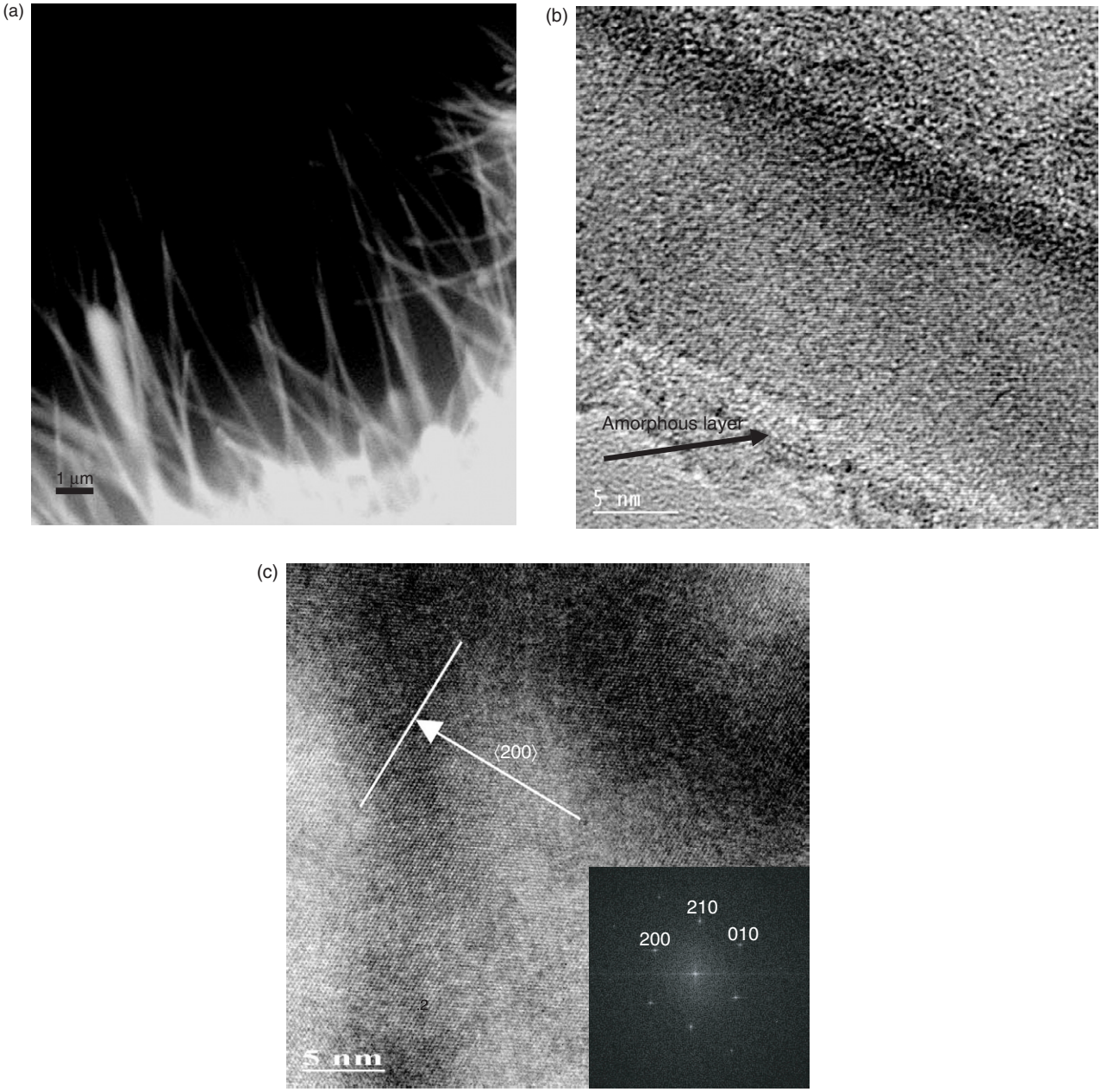

Figure 2. (*a*) TEM image in cross-section view. Inset reveals the chemical composition of a single TiO_2 nanowire. (*b*) The HRTEM image of a single TiO_2 nanowire coated with an amorphous layer. (*c*) HRTEM image of a single TiO_2 nanowire. The growth direction is along the ⟨200⟩ direction.

single crystalline TiO_2 nanowire arrays aligned on Si wafers prepared through a simple vapour phase deposition (PVD) method. To the best of our knowledge, this is the first report on both template-free physical vapour deposition (PVD) synthesis of TiO_2 nanowire arrays on Si wafers and their field emission properties.

2. Experimental details

The TiO_2 nanowire arrays were prepared through a simple PVD method. The synthesis process was carried out in a conventional alumina tube furnace. First, an n-doped Si wafer was put on a quartz boat loaded with pure Ti metal powder (99.0%, 2 g), which served as the titanium source. The distance between the substrate and source was kept at ∼0.5 mm. The boat was then transferred into the furnace. Before TiO_2 nanowire growth, the furnace chamber was pumped and purged with high purity argon gas, three times. Then, the temperature was increased to 850°C under the protection of an argon gas flow. Subsequently, the chamber was pumped down to ∼300 Torr and the flow rate of the argon gas was set at 100 sccm and held for 3 h. When the reaction was completed, a layer of black material was observed deposited on the surface of the Si wafer. It is noted that a change in the

growth conditions such as the reaction time and the position of the substrate can result in a peculiar SiO_2/TiO_2 shell/core nanostructure [16]. The morphology of the as-synthesized products was examined by scanning electron microscopy (SEM). Their microstructure and chemical composition were analysed by transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS), respectively. The field emission measurements were carried out in a homemade system in a high vacuum chamber. The emission current was monitored using a 485 Keithley meter.

3. Results and discussions

The morphology of the TiO_2 nanowires was examined by SEM. As shown in figure 1, vertically aligned nanowires with high density were found deposited on the entire surface of the Si substrate. Figure 2(*a*) shows a cross-sectional TEM view of nanowires grown directly on the surface of the substrate, which shows that the growth of TiO_2 nanowires followed a base-up growth process. The TiO_2 nanowires have a smooth surface and possess an almost unique diameter as illustrated in the TEM image in figure 2(*a*). The length and diameter of the TiO_2 nanowires were about 15 μm and 100 nm, respectively. Detailed TEM analysis further revealed that the nanowires are actually coated with an amorphous layer as shown in figure 2(*b*). An high-resolution transmission electron microscopy (HRTEM) image shows that the TiO_2 nanowires are single crystalline (figure 2(*c*)). The corresponding fast Fourier transformation (FFT) shown in the inset confirms the single-crystal nature of the TiO_2 nanowire. Detailed FFT analysis reveals that the growth direction of the as-synthesized TiO_2 nanowires is along the ⟨200⟩ direction. EDS analysis indicated that the as-synthesized products consist of Ti and O elements with a component ratio equal to 1 : 2. The oxygen element originate from the residual O_2 gas leaked into the chamber.

Because no metal-catalysts were used in the source materials, the growth mechanism of the TiO_2 nanowires cannot be explained by a conventional vapour–liquid–solid (VLS) model [17]. We proposed the following process which is similar to the model described in [18] to explain the growth of TiO_2 nanowires evolving a Si–Ti alloy: at the beginning, the Si substrate was surrounded by O and Ti species in the reaction chamber. Subsequently, the O and Ti species dissolved into the Si and formed complex nano-sized Si–O–Ti alloy islands on an Si–Ti alloy film. Continuous feeding of Ti and O into the quasi-liquid Si–Ti–O nanoislands leads to one-dimensional growth of TiO_2 single crystals with a process similar to that in a VLS model.

Room temperature field emission measurements were performed in a high-vacuum chamber (10^{-7} Pa). The n-type Si substrate was employed as a cathode. The distance between the anode and the tips of the TiO_2 nanowires was 150 μm. The measured emission area was 1.84 mm^2, estimated by an optical microscope observation. The emission current was recorded by changing the voltage at a step of 50 V. The field emission I–V curves were analysed using the Fowler–Nordheim (FN) equation for the field emission:

$$J = A\left(\frac{\beta^2 V^2}{\phi d^2}\right)\exp\left(\frac{-B\phi^{3/2}d}{\beta V}\right),$$

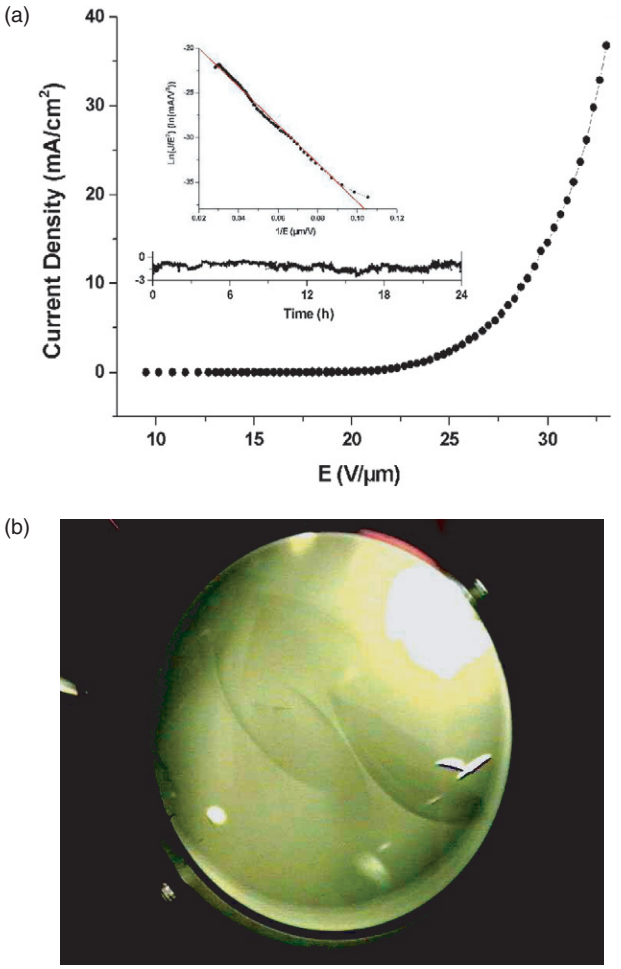

Figure 3. (*a*) The field emission current density versus electric field characteristic of the TiO_2 nanowire arrays. The upper inset shows the corresponding FN plot of the sample. The middle inset shows the stability of the emission current. (*b*) Fluorescence image of field emission from the TiO_2 nanowire arrays.

(This figure is in colour only in the electronic version)

where ϕ is the work function, J is the current density, $A = 1.56 \times 10^{-10}$ (A V^{-2} eV), $B = 6.83 \times 10^9$ (V eV$^{-3/2}$ m^{-1}), β denotes the field enhancement factor, $E = (V/d)$ is the applied field, d is the distance between the anode and the cathode and V is the applied voltage [11]. Figure 3(*a*) shows the emission current density from the TiO_2 nanowire arrays on the Si substrate. Our experimental results show that the emission current is very stable and has no obvious change over a period of 24 h at a current density of 1.5 μA cm^{-2} (inset, figure 3(*a*)). The turn-on voltage was about 13 V μm^{-1}, corresponding to a current density of 0.1 μA cm^{-2}. The emission current density reached about 1 mA cm^{-2} at an applied field of about 23 V μm^{-1} (the so-called threshold field). The FN plot is also shown in the inset of figure 3(*a*). It indicates a linear behaviour in the measurement range. So the emission is indeed attributed to a vacuum tunnelling process. Figure 3(*b*) is the cathode-luminescence image recorded using a CCD camera of the fluorescence of a phosphor screen at daylight at an accelerating voltage of 4 kV. As supported by this image, the luminescence observed under daylight is very

bright and homogeneous. To sum up, the TiO_2 nanowire array based cold-cathodes had all the desirable characteristics of a flat panel display such as its picture quality, brightness and stability.

4. Conclusions

In conclusion, vertically aligned single crystalline TiO_2 nanowire arrays were successfully deposited on an n-doped Si wafer using a simple PVD method. The high purity of TiO_2 arrays was attained by our vapour phase approach. The field emission from TiO_2 nanowire arrays is efficient and stable. The emission current value from TiO_2 nanowires could produce sufficient brightness for flat panel displays. Since the TiO_2 is more chemically stable than CNT, it has a potential future in the flat panel display and vacuum microelectronics industry. Application of TiO_2 nanowire arrays should not be limited to vacuum microelectronics. They also seem to have considerable potential for fabrication of optical and electro-optical devices. For example, organic-dye sensitive TiO_2 nanowire arrays can be used to construct solar-energy conversion devices because of their high specific surface area and aligned configuration as well as due to their single crystalloid.

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References

[1] Wu Z S, Deng S Z, Xu N S, Chen Jian, Zhou J and Chen Jun 2002 *Appl. Phys. Lett.* **80** 3829
[2] Zhou J, Deng S Z, Xu N S, Chen Jun and She J C 2003 *Appl. Phys. Lett.* **83** 2653
[3] Zhu Y W, Zhang H Z, Sun X C, Feng S Q, Xu J, Zhao Q, Xiang B, Wang R M and Yu D P 2003 *Appl. Phys. Lett.* **83** 144
[4] Lee C J, Lee T J, Lyu S C, Zhang Y, Ruh H and Lee H J 2002 *Appl. Phys. Lett.* **81** 3648
[5] Wan Q, Yu K, Wang T H and Lin C L 2003 *Appl. Phys. Lett.* **83** 2253
[6] Jia H B, Zhang Y, Chen X H, Shu J, Luo X H, Zhang Z S and Yu D P 2003 *Appl. Phys. Lett.* **82** 4146
[7] Adachi H, Fujii K, Zaima S and Shibata Y 1983 *Appl. Phys. Lett.* **43** 702
[8] Fan S S, Chapline M G, Franklin N R, Tombler T W, Cassell A M and Dai H J 1999 *Science* **283** 512
[9] Dean K A and Chalamala B R 2000 *Appl. Phys. Lett.* **76** 375
[10] Bonard J M, Maier F, Stockli T, Chatelain A, de Heer W A, Salvetat J P and Forro L 1998 *Ultramicroscopy* **73** 7
[11] Araki H, Katayama T and Yoshino K 2001 *Appl. Phys. Lett.* **79** 2636
[12] Gao R, Pan P Z and Wang Z L 2001 *Appl. Phys. Lett.* **78** 1757
[13] Caruso R A, Schattka J H and Greiner A 2001 *Adv. Mater.* **13** 1577
[14] Zhang Y X, Li G H, Jin Y X, Zhang Y, Zhang J and Zhang L D 2002 *Chem. Phys. Lett.* **365** 300
[15] Lei Y, Zhang L D, Meng G W, Li G H, Zhang X Y, Liang C H, Chen W and Wang S X 2001 *Appl. Phys. Lett.* **78** 1125
[16] Zhang H Z, Luo X H, Wang R M, Xu J, Xiang B and Yu D P Synthesis of TiO_2/SiO_2 core/shell nanocable arrays unpublished
[17] Xu C K, Zhan Y J, Hong K Q and Wang G H 2003 *Solid State Commun.* **126** 545
[18] Lyu S C, Zhang Y, Ruh H, Lee H J and Lee C J 2003 *Chem. Phys. Lett.* **367** 717