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# Electron field emission from well-aligned GaP nanotips

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Field emission of electrons from single crystal gallium phosphide (GaP) nanotips has been investigated. GaP nanotip arrays were fabricated using silane-methane-argon-hydrogen based plasma using the self-masking dry etching technique in an electron-cyclotron-resonance microwave plasma enhanced chemical vapor deposition system. These nanotips have an average of 2 and 80 nm in apex and bottom diameters, respectively. They are 900 nm in height, which makes them the perfect electron emission source for their high aspect ratio topography. A nanosized silicon carbide (SiC) cap on each GaP nanotip in the array has been found. The SiC core has a heterointerface with GaP crystal that was observed using a high resolution transmission electron microscope. Field emission analysis shows low turn-on fields of 8.5–9 V/ $\mu\text{m}$ . Cold electron emissions in Fowler–Nordheim type current-voltage were observed from such GaP nanotip arrays. © 2010 American Vacuum Society. [DOI: 10.1116/1.3506089]

## I. INTRODUCTION

Because of their fascinating optical, mechanical, and electrical properties, the synthesis of wide band gaps with one-dimensional (1D) nanostructure materials has attracted much attention.<sup>1–3</sup> Among these compound semiconductor nanostructures, GaP is a promising candidate for potential applications in areas involving optoelectronics. It has been highly considered due to its green-light emission, electronic conductivity, and electronic transportation properties. As single crystal GaP substrates can also be used as an essential template for synthesizing indium gallium phosphide (InGaP) and gallium arsenide (GaAs) materials for optoelectronic applications,<sup>4,5</sup> its synthesis and applications on 1D nanostructures has yet to be investigated thoroughly.

Development of novel materials as cold cathode emitters for large area field emission array in display application has been extensively investigated in recent years. Low operating voltage with high stability in emission current densities are the basic requirements for field emission displays undergoing commercialization. For this unique application, the 1D nanostructure has become an important candidate for use in stable field emitters, owing to its high aspect ratio structure with variable conductivity by doping impurities. There were reports of emitters having different forms and compositions, such as carbon nanotubes (CNTs),<sup>6–10</sup> carbon nanotips,<sup>11</sup> silicon nanocone,<sup>12</sup> silicon nanotips,<sup>13</sup> ZnO nanorod,<sup>14</sup> and silicon carbon nitride (SiCN) nanorods<sup>15</sup> that compete for supremacy. Recent theoretical study has also enabled the

modification of the classic thick-slab barrier to a thin-slab model to explain the electron emission from the emitter with the apex in nanometer size or even in atomic scale instead of flat surfaces.<sup>16</sup> However, preparing such nanostructures to be uniform over a large area and simultaneously control the topography of these nanostructures is difficult to achieve.<sup>12</sup> One of the common techniques for fabricating 1D nanostructure for field emission devices is the chemical vapor deposition (CVD) process that utilizes the vapor-liquid-solid mechanism to grow nanostructures (bottom-up technique). It should be emphasized that the inherent adhesion problem and the complexity of the deposition process of most of these nanostructures lead to a problematic integration into the selective sites and heterogeneous substrates<sup>17</sup> in the ultimate device production process. Our approach (top-down) eliminates these adhesion problems and inherent substrate preferences since the nanotip arrays can be directly etched from a wide range of semiconductor substrates.<sup>13</sup>

## II. EXPERIMENT

The one-step fabrication of semiconductor nanotip arrays using a large area etching technique has been demonstrated using single crystal silicon substrate<sup>13</sup> and silicon carbide films.<sup>15</sup> Therefore, we use GaP wafers with a similar technique to prepare these nanotip arrays. A 1.5 kW AsTex AX2115 microwave source and an AX4400 electromagnet were employed to generate the high-density electron cyclotron resonance (ECR) plasma. The plasma is composed of a mixture of semiconductor-grade gases, silane (SiH<sub>4</sub>), methane (CH<sub>4</sub>), argon (Ar), and hydrogen (H<sub>2</sub>), with typical flow rates of 0.2, 3, 3, and 8 SCCM (SCCM denotes cubic centi-

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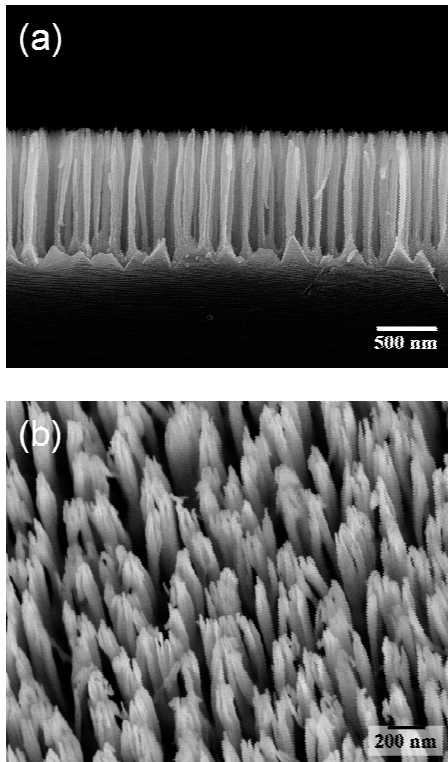


FIG. 1. HRSEM image of (a) the cross-sectional view of the GaP nanotip array and (b) from the 25° tilted image of ultrasharp GaP nanotip array.

meter per minute at STP), respectively. The gas mixture at a pressure of 3.2 mTorr was ionized directly by a microwave energy source (typically 1200 W) under a high electromagnetic field (875 G). Without any pretreatment or any catalyst coating, the reaction begins on a pure GaP substrate in the size of  $1 \times 2$  cm<sup>2</sup> cut from a GaP wafer. The substrate temperature for fabricating GaP nanotip arrays can vary between 150 and 800 °C, and can be detected by a thermocouple attached directly to the substrate holder. The GaP nanotip array with a SiC cap starts developing under the active etching and codeposition of the high-density plasma.

High resolution scanning electron microscopy (HRSEM, JEOL JSM-6700 field emission scanning electron microscope) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-3000F) were used to study both the morphological and structural aspects of the bare GaP nanotip array distribution, respectively. The field emission measurement system we used was a laboratory-assembled vacuum chamber pumped by a turbo molecular pump (Alcatel, ATP-400). A Windows-based data acquisition program combined with a Keithley 237 power supply was used to detect the field emission currents with voltages in this study. To estimate the reliable current density versus applied field ( $J$ - $V$ ) results, the pressure of measurement was maintained under  $5 \times 10^{-7}$  Torr regime.

### III. RESULT AND DISCUSSION

Figures 1(a) and 1(b) show typical HRSEM cross-sectional and 25° tilted images of GaP nanotips, respectively.

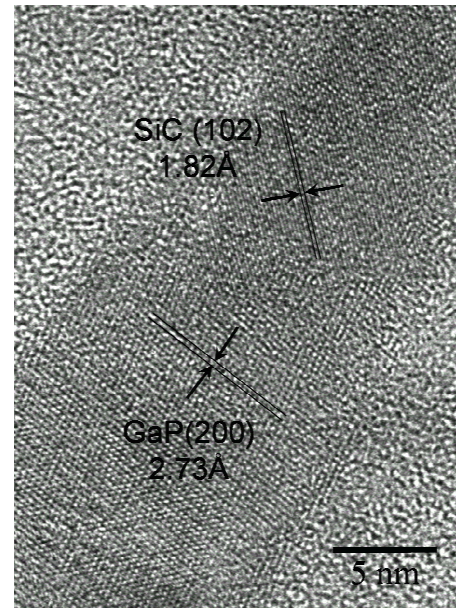


FIG. 2. HRTEM image of a single GaP nanotip capped with a SiC core formation on top of the tip.

The SEM image [Fig. 1(a)] indicates that the nanotips fabricated by ECR-CVD are 2 and 80 nm in diameter at the apex and bottom of the nanotips, respectively. They are 900 nm in height, which gives an aspect ratio approaching 11.25. The 25° tilted plane view SEM image, as shown in Fig. 1(b), exhibits a uniform distribution with a high density of  $2 \times 10^{11}/\text{cm}^2$  of the GaP nanotip array. Compared to porous  $n$ -GaAs fabricated using the anodic wet etching method,<sup>14</sup> the well-aligned high aspect ratio GaP nanotip array is a good candidate for field electron emission applications.

The HRTEM image, as shown in Fig. 2, clearly demonstrates the heterostructure aspects of the individual SiC capped GaP nanotip distribution. The HRTEM image shows the GaP structure with a (200) lattice spacing of 2.73 Å at the body of the nanotip array. The structure on the top of the tip with a lattice spacing of 1.82 Å is a close match to the literature report of the 2H-SiC (102) structure.<sup>18</sup> The SiC nanoprotectors were formed on the GaP substrate using a combination of dissociated silane and methane gases. Subsequently, etching progresses on the GaP substrate under an argon and hydrogen plasma environment. The particular etching mechanism and the detailed structural identification of the nanotip array have been discussed in a separate article.<sup>19</sup>

The field emission property was measured in a high vacuum system with a base pressure of  $5 \times 10^{-7}$  Torr. Curve I in Fig. 3(a) shows the  $J$ - $V$  characteristics of the GaP nanotip array with the cathode-to-anode distance of 30 μm. The current density was 10 μA/cm<sup>2</sup> at an applied voltage of 255 V, which corresponds to an applied turn-on field of 8.5 V/μm. The corresponding Fowler–Nordheim (FN) plot of curve I was shown in Fig. 3(b)-I, depicting the linear behavior typical of field emission action. Subsequent to the above measurement of 30 μm cathode-to-anode distance,

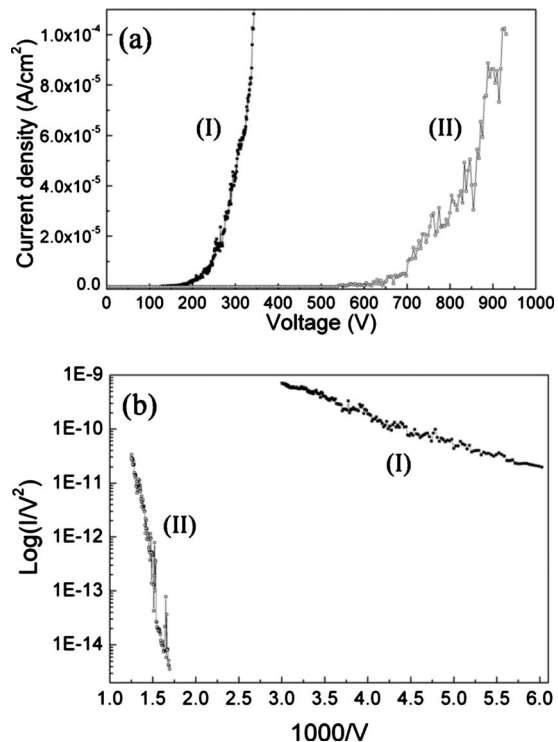


FIG. 3. Field emission characteristics of the GaP nanotip array. (a) The  $J$ - $V$  characteristics of the nanotip array with (I) 30 and (II) 80  $\mu\text{m}$  of cathode-to-anode distance. (b) The corresponding Fowler-Nordheim plot from (I) and (II).

we changed the cathode-to-anode distance to 80  $\mu\text{m}$  to compare the field emission characteristics with the 30  $\mu\text{m}$  one. The results of a field emission measurement in the 80  $\mu\text{m}$  cathode-to-anode distance configuration are shown in Fig. 3(a)-II. The applied turn-on voltage required to extract a current density of 10  $\mu\text{A}/\text{cm}^2$  was 8.875 V/ $\mu\text{m}$ , which is close to that measured with a 30  $\mu\text{m}$  cathode-to-anode gap. Such differences in turn-on voltage using various cathode-to-anode distances were also observed in other types of cold cathode emitters, such as CNTs,<sup>20</sup> nanowires,<sup>21</sup> and carbon nitride ( $\text{C}_x\text{N}_y$ ) film.<sup>22</sup> As shown in Fig. 3(b)-II, although the anode-cathode spacing was increased, the representative FN measurement also possessed linear activities for a typical field emission behavior. The reproducibility of the  $J$ - $V$  characteristic and the nature of the FN plot were repeatedly confirmed. Hence, GaP is established as a potential field emitter in the same queue as those of carbon nanotubes and other 1D nanostructures.

#### IV. CONCLUSIONS

In summary, a one-step fabrication method with high uniformity of the GaP nanotip array synthesized over a large area by the ECR-CVD technique has been achieved. In the

ECR plasma environment, SiC nanoprotectors were formed from the silane and methane gas reaction. In the meantime, the phenomenon of physical sputtering and chemical etching was caused by argon and hydrogen plasmas, respectively, which resulted in the nanotip formation. This technique has the advantages of a relatively simple fabrication process compared with the epitaxial growth and general applicability in a number of semiconductor wafers. It also has the advantage in compatibility with well-established semiconductor processes.

The field emission properties of the GaP nanotip array demonstrate low turn-on fields of 8.5 and 8.875 V/ $\mu\text{m}$  for cathode-to-anode distances of 30 and 80  $\mu\text{m}$ , respectively. Stable field emission properties and the large area production make the GaP nanotip array a potentially viable field-emitting material for industrial applications.

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