intermittent etching practices are contemplated. Etching may be performed upon one or more faces, or upon a portion or all surfaces of a silicon carbide substrate.

[0035] As silicon carbide is a polar material, there is an internal electric field which results in differences in etch results on the two faces of the wafer. These two faces, referred to as the "Si-face" and the "C-face" are capable of field emission, and the emitter device may be comprised of either face of the wafer. The specific built-in field, characteristic of one or the other face, may have advantages depending on the specific application. As a result one face may have preferential emission properties over the other.

[0036] The electrolyte or anodizing solution used in the electrochemical etching generally includes at least one reducing agent, at least one oxidizer, and water which may act as an oxidizer. The agents may work in conjunction with the applied voltage present in the electrochemistry process. The solution may also include one or more additional components or be limited to the three noted components. A wide array of reducing agents can be used in the anodizing solution such as for example acidic reducing agents. A preferred reducing agent is hydrofluoric acid which can be used at a concentration of from about 1% to about 30%, with typical concentrations being 10% or 20%. A wide array of oxidizers can be used in the anodizing solution such as for example one or more alcohols. A preferred oxidizer is ethanol which can be used at a concentration of from about 5% to about 30%, with 5% being preferred for many applications. Other oxidizers may be acid-based such as nitric acid, or other alcohols such as methanol. The anodizing solution also includes water. The water can be deionized water or distilled water for example. For certain applications, deionized water is preferred because deionized water typically contains fewer contaminants. Such contaminants can produce or lead to undesirable by-products during electrochemical etching. Furthermore, deionized water is less electrically conductive than distilled water and tends to produce a more ordered pore structure. When forming field emitters, typically a relatively ordered pore structure is preferred as compared to a more random pore structure.

[0037] The electrochemical etching operation(s) can be performed at ambient temperatures, which are generally considered to be within a range of from about 65° F. (18° C.) to about 75° F. (24° C.).

[0038] The electrochemical etching operations(s) may be assisted by illumination with incident light of sufficiently large photon energy, so as to promote the anodization process.

[0039] Similar electrochemical etching processes are described in Ke, Y., Devaty, R. P. & Choyke, W. J., Comparative Columnar Porous Etching Studies on N-Type 6H SiC Crystalline Faces, *Phys. Stat. Sol*. (b) 245, 1396-1403 (2008); and Ke, Y., Devaty, R. P. & Chjoyke, W. J., Self-Ordered Nanocolumnar Pore Formation in the Photoelectrochemical Etching of 6H SiC. *Electrochem, Solid-State Lett.* 10, K24-K27 (2007).

[0040] After subjecting the silicon carbide substrate to electrochemical etching, the substrate is rendered porous, with porosity ranging from 50% to 98%. In certain versions of the present subject matter, the porosity of the substrate can be characterized as nanoporous. The term "nanoporous" as used herein refers to a structure in the silicon carbide substrate that includes numerous pore walls which have a size generally within the nanometer range. Additional details and characteristics of the porous silicon carbide structure are provided herein.

[0041] The methods of the present subject matter also include one or more operations for forming the discrete emission projections extending from a face of the porous silicon carbide substrate. The operations preferably include for example, one or more ion etching operations which are performed after the electrochemical etching. Non-limiting examples of ion etching operations include focused ion beam (FIB) etching which may be gas-assisted, and reactive ion etching (RIE). Generally, both of these types of ion etching operations can be performed at room temperature.

[0042] Focused ion beam etching is a technique used particularly in the semiconductor industry, materials science and increasingly in the biological field for site-specific analysis, deposition, and ablation of materials. A wide variety of systems for performing focused ion beam etching or milling are known in the art and/or are commercially available.

[0043] Reactive ion etching technology is typically used in microfabrication. This technique uses chemically reactive plasma to remove material deposited on a substrate or wafer. A plasma is generated under low pressure (vacuum) by an electromagnetic field. High energy ions from the plasma attack the wafer surface and react with the surface. Similarly, a wide array of reactive ion etching systems are known and are commercially available.

Field Emitters

[0044] The silicon carbide field emitters of the present subject matter exhibit certain characteristics as follows. In certain versions, the field emitters include a collection of discrete emission projections such as pillars, fins, or columns, extending from one or more faces or portion(s) of a face. The emission projections typically have an average height within a range of from about 1 micron to about 100 microns, an average thickness of from about 0.01 microns to about 10 microns, and an average spacing of from about 1 micron to about 100 microns. However, it will be understood that the present subject matter includes emitters having emission projections with heights, thicknesses, and/or spacings different than these representative ranges.

[0045] The field emitters are relatively porous and typically exhibit an average pore wall thickness of from about 10 nm to about 1,000 nm, and an average pore size of from about 10 nm to about 1,000 nm. Similarly and as noted, the present subject matter includes substrates and emitters having different pore sizes and pore wall thicknesses.

[0046] A significant benefit of the present subject matter field emitters is that the field emitters are monolithic and specifically, porous. As the porous structure is fabricated by removal of material, the remaining structure is compositionally homogenous and free of interfaces with other materials, such that the structure provides a continuous supply of emitter material. Thus, the porous, homogenous, and monolithic structure provides emitters which are reliable and exhibit a relatively long lifetime. The field emitters are monolithic and homogenous in a direction transverse to the emission face of the field emitter. This aspect refers to a characteristic of the emitter in which the emitter structure, i.e. between the emission face and an oppositely directed rear face, is free of any other materials or material layers besides silicon carbide. Thus, the emitter structure is free of any material interfaces along or proximate the emission face. And therefore in many versions of the present subject matter, the emitter structure consists entirely of silicon carbide and particularly porous silicon carbide. It will be understood that one or more elec-