DISCLOSURE OF INVENTION

[0012] In order to address the above identified limitations in the art, there are provided various methods and apparatuses for a multi-needle parallel nanospray ionization source for mass spectrometry. The inventors of embodiments of the present invention have realized assemblages of microstructures similar to those described by Oleinikov et al. could be advantageously employed as nano-electrospray emitter arrays. Accordingly, the structure, fabrication and use of such ionization sources are disclosed herein.

[0013] In a first aspect, there is provided an electrospray ion source for a mass spectrometer characterized by: an electrode comprising at least a first plurality of protrusions protruding from a base, each protrusion of the at least a first plurality of protrusions having a respective tip; a conduit for delivering an analyte-bearing liquid to the electrode; and a voltage source, wherein, in operation of the electrospray ion source, the analyte-bearing liquid is caused to move, in the presence of a gas or air at a pressure within the range of 0.03 × to 2 × atmospheric pressure, from the base to each protrusion tip along a respective protrusion exterior so as to form a respective stream of charged particles emitted towards an ion inlet aperture of the mass spectrometer under application of voltage applied to the electrode from the voltage source. In an embodiment~~a first aspect~~ of the invention, there is disclosed an electrospray ion source for a mass spectrometer comprising: an electrode comprising at least a first plurality of protrusions protruding from a base, each protrusion of the at least a first plurality of protrusions having a respective tip; a conduit for delivering an analyte-bearing liquid to the electrode; and a voltage source, wherein, in operation of the electrospray ion source, the analyte-bearing liquid is caused to move, in the presence of a gas or air, from the base to each protrusion tip along a respective protrusion exterior so as to form a respective stream of charged particles emitted towards an ion inlet aperture of the mass spectrometer under application of voltage applied to the electrode from the voltage source. The first plurality of protrusions may occupy an area of the electrode having a shape that corresponds to a shape of the ion inlet aperture. Various embodiments may comprise a coating layer adhered to at least a portion of each of the protrusions, the coating layer providing an increase in a tendency of the analyte-bearing liquid to be drawn towards the protrusion tips. Various embodiments may comprise an extractor electrode spaced at a distance from the electrode so as to form a gap therebetween, the extractor electrode having an aperture therein such that, in operation of the electrospray ion source, an electric field between the electrode and the extractor electrode causes a portion of the emitted charged particles to be propelled through the aperture in the extractor electrode. Various embodiments may comprise a bottom substrate adhered to a side of the electrode opposite to the protrusions so as to provide structural support to the electrode. Various embodiments may comprise a cover plate having at least one aperture therein; and a spacer disposed between the cover plate and the base of the electrode, so as to form a gap between at least a portion of the cover plate and at least a portion of the electrode, such that analyte-bearing liquid delivered from the conduit is caused to flow into the gap, wherein the first plurality of protrusions protrude through the at least one aperture.

[0014] In a second aspect, there is provided a method of fabricating a multi-emitter electrospray electrode comprising the steps of (a) providing a substrate; (b) exposing a first side of the substrate to a beam of accelerated heavy ions so as to produce a set of latent ion tracks within the substrate that do not penetrate to an opposite side of the substrate; (c) exposing the first side of the substrate to a chemical etchant so as to form a plurality of etch channels within the substrate that extend into the substrate interior from the first side of the substrate; and (d) depositing a layer of conductive material within the etch channels and on the first side of the substrate, the conductive material deposited within the etch channels comprising a plurality of conical pillars having tips, the method characterized by: (e) removing a portion of an opposite side of the substrate and at least a portion of the tips of the conical pillars so as to truncate a subset of the plurality of conical pillars, the truncated conical pillars comprising hollow electrospray nozzles of the multi-emitter electrospray electrode. In other embodiments~~aspects~~ of the invention, there are disclosed methods of fabricating a multi-emitter electrospray electrode including the steps of: providing a substrate; exposing a first side of the substrate to a beam of accelerated heavy ions so as to produce a set of latent ion tracks within the substrate that do not penetrate to an opposite side of the substrate; exposing the first side of the substrate to a chemical etchant so as to form a plurality of etch channels within the substrate that extend into the substrate interior from the first side and that do not penetrate to the opposite side of the substrate; and depositing a layer of conductive material within the etch channels and on the first side of the substrate. Alternative subsequent steps may include either removing the substrate from the conductive material, the conductive material comprising the multi-emitter electrospray electrode or removing a portion of the opposite side of the substrate and at least a portion of the tips of the conical pillars so as to truncate a subset of the plurality of conical pillars, the truncated conical pillars comprising hollow electrospray nozzles of the multi-emitter electrospray electrode.

[0015] In a third aspect, there is provided a method for providing ions derived from an analyte-bearing liquid to a mass spectrometer by electrospray ionization, the analyte-bearing liquid supplied at a total flow rate of greater than or equal to 50 microliters (μl) per minute characterized by: (a) dividing the total flow into a plurality of sub-flows of analyte-bearing liquid, each sub flow providing a portion of the total flow at a rate of less than or equal to 500 nanoliters (nl) per minute; (b) providing a plurality of electrospray emitters; (c) providing each sub-flow of analyte bearing liquid to a respective one of the electrospray emitters; (d) generating an electrospray emission from each of the electrospray emitters; and (e) directing each electrospray emission to an ion inlet of the mass spectrometer. In yet other embodiments~~aspects~~ of the invention, there are disclosed methods for providing ions derived from an analyte-bearing liquid to a mass spectrometer by electrospray ionization, the analyte-bearing liquid supplied at a total flow rate of greater than or equal to 50 microliters (μl) per minute comprising: (a) dividing the total flow into a plurality of sub-flows of

analyte-bearing liquid, each sub flow providing a portion of the total flow at a rate of less than or equal to 500 nanoliters (nl) per minute; (b) providing a plurality of electrospray emitters; (c) providing each sub-flow of analyte bearing liquid to a respective one of the electrospray emitters; (d) generating an electrospray emission from each of the electrospray emitters in the presence of a gas or air; and (e) directing each electrospray emission to an ion inlet of the mass spectrometer. The gas or air, which may be at atmospheric pressure in various embodiments, may provide controllable evaporation of a solvent or aid in de-clustering between analyte ions and other particles. In other embodiments, the gas or air may be maintained at a pressure within a range of 0.03 × atmospheric pressure to 2 × atmospheric pressure.

[0016] Apparatus in accordance with the present teachings can comprise a material that has a large number of pillars per unit area – typically 1000-500,000 per square centimeter, corresponding to an average inter-pillar spacing in the range of approximately 6-320 μm. The tips of the pillars, from which ions are emitted when the electrode is in use as an