

236 on the ejection side of the silicon substrate exposing the underlying silicon substrate 220.

[0116] FIG. 15H is a cross-sectional view of a silicon substrate 200 showing removal of silicon substrate 220 to form an annular space 240 around the nozzles 242.

[0117] FIG. 15I is a cross-sectional view of the DRIE etch of silicon 220 to form the recessed annular region 240 and the nozzles 242.

[0118] FIG. 15J is a cross-sectional view of a silicon substrate 200 showing removal of silicon dioxide layers 210, 212, 233 and 238.

[0119] FIG. 16A is a cross-sectional view of a silicon substrate 200 showing thermal oxidation of the exposed silicon substrate 200 to form a layer of silicon dioxide 244 on all exposed silicon surfaces.

[0120] FIG. 16B is a cross-sectional view of a silicon substrate 200 showing low pressure vapor deposition of silicon nitride 246 conformally coating all exposed silicon surfaces.

[0121] FIG. 16C is a cross-sectional view of a silicon substrate 200 showing deposition of layers of conductive metal 247, 248.

[0122] FIG. 17A is a cross-sectional view of a silicon substrate 200 showing the reservoir 232 and through-wafer channels 242 filled with a polymerizable solution 252. The polymerizable solution 252 is contained within the device with coverplates 248.

[0123] FIG. 17B is a cross-sectional view of a silicon substrate 200 showing the reservoir 232 and through-wafer channels 242 filled with polymer monolith 254.

[0124] FIG. 18 is a cross-sectional view of a two nozzle polymer monolith/electrospray device of the present invention 250 showing metal deposition of electrode 256 on silicon substrate 200.

[0125] FIGS. 19A and 19B show a perspective view of scanning electron micrograph images of a multi-nozzle device fabricated in accordance with the present invention.

[0126] FIG. 20A shows two stacked separation blocks each having a plurality of separation channels filled with a porous polymeric material.

[0127] FIG. 20B shows a separation block having a separation channel filled with a porous polymeric material stacked on an electrospray device.

#### DETAILED DESCRIPTION OF THE INVENTION

[0128] Control of the electric field at the tip of a nozzle is an important component for successful generation of an electrospray for microfluidic microchip-based systems. This invention provides sufficient control and definition of the electric field in and around a nozzle microfabricated from a monolithic silicon substrate for the formation of multiple electrospray plumes from closely positioned nozzles. The present nozzle system is fabricated using Micro-ElectroMechanical System ("MEMS") fabrication technologies designed to micromachine 3-dimensional features from a silicon substrate. MEMS technology, in particular, deep reactive ion etching ("DRIE"), enables etching of the small

vertical features required for the formation of micrometer dimension surfaces in the form of a nozzle for successful nano-electrospray of fluids. Insulating layers of silicon dioxide and silicon nitride are also used for independent application of an electric field surrounding the nozzle, preferably by application of a potential voltage to a fluid flowing through the silicon device and a potential voltage applied to the silicon substrate. This independent application of a potential voltage to a fluid exiting the nozzle tip and the silicon substrate creates a high electric field, on the order of  $10^8$  V/m, at the tip of the nozzle. This high electric field at the nozzle tip causes the formation of a Taylor cone, fluidic jet and highly-charged fluidic droplets characteristic of the electrospray of fluids. These two voltages, the fluid voltage and the substrate voltage, control the formation of a stable electrospray from this microchip-based electrospray device.

[0129] The electrical properties of silicon and silicon-based materials are well characterized. The use of silicon dioxide and silicon nitride layers grown or deposited on the surfaces of a silicon substrate are well known to provide electrical insulating properties. Incorporating silicon dioxide and silicon nitride layers in a monolithic silicon electrospray device with a defined nozzle provides for the enhancement of an electric field in and around features etched from a monolithic silicon substrate. This is accomplished by independent application of a voltage to the fluid exiting the nozzle and the region surrounding the nozzle. Silicon dioxide layers may be grown thermally in an oven to a desired thickness. Silicon nitride can be deposited using low pressure chemical vapor deposition ("LPCVD"). Metals may be further vapor deposited on these surfaces to provide for application of a potential voltage on the surface of the device. Both silicon dioxide and silicon nitride function as electrical insulators allowing the application of a potential voltage to the substrate that is different than that applied to the surface of the device. An important feature of a silicon nitride layer is that it provides a moisture barrier between the silicon substrate, silicon dioxide and any fluid sample that comes in contact with the device. Silicon nitride prevents water and ions from diffusing through the silicon dioxide layer to the silicon substrate which may cause an electrical breakdown between the fluid and the silicon substrate. Additional layers of silicon dioxide, metals and other materials may further be deposited on the silicon nitride layer to provide chemical functionality to silico-based devices.

[0130] Arrays of multiple electrospray nozzles of any nozzle number and format may be fabricated according to the present invention. FIG. 1A illustrates a two by two array of groups of four electrospray nozzles for one common fluid stream. FIG. 1A shows a perspective view of the ejection or nozzle side a four-nozzle electrospray device array 250 of the present invention. Each recessed annular region 240 has four nozzles 242 that generate one or more electrosprays for the same fluid stream introduced to a reservoir containing a polymer monolith on the injection side of the device. Each device has a group of four electrospray nozzles in fluid communication with one common reservoir containing a single fluid sample source. Thus, this system can generate multiple sprays for each fluid stream up to four different fluid streams. An electrode 256 is placed on the silicon substrate 200 for application of a potential voltage to the substrate.