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(54) **Silicon nozzle structures and method of manufacture.**

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(73) Proprietor : **AT & T Teletype Corporation**  
**5555 Touhy Avenue**  
**Skokie Illinois 60077 (US)**

(72) Inventor : **Waggner, Herbert A.**  
**3 Half Day Road**  
**Lincolnshire Illinois 60060 (US)**  
Inventor : **Zuercher, Joseph C.**  
**235 Catalpa Place**  
**Wilmette Illinois 60091 (US)**

(74) Representative : **Blumbach Weser Bergen**  
**Kramer Zwirner Hoffmann Patentanwälte**  
**Sonnenberger Strasse 100**  
**D-65193 Wiesbaden (DE)**

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## Description

### Technical Field

5 Monocrystalline silicon bodies with passages.

### Background of the Invention

10 In the prior art and specifically in US-A-3,921,916 it is suggested that a monocrystalline, crystallographically oriented silicon wafer may be selectively etched to form one or more reproducible channels of a specific form in the wafer body. The specific type of the channel described in that patent has a rectangular entrance cross-section which continues to an intermediate rectangular cross-section, smaller than the entrance cross-section, and then to an exit cross-section which has a shape other than rectangular. A channel of this specific type is established by either of two disclosed processes, both of which utilize a heavily doped p+ layer (patterned in the one process and unpatterned in the other) as an etchant barrier. In the two processes, a silicon  
15 wafer is heavily doped to place it near or at saturation from one major face to form the p+ etchant barrier. Thereafter, patterned anisotropic etching from the opposite major face proceeds until the p+ barrier is reached. The anisotropic etching results in a rectangular entrance cross-section and a rectangular intermediate cross-section defining a membrane smaller in size than the entrance cross-section.

20 In the application of one process, the etching Process is continued from the entrance side until an opening is made through the membrane. The other process utilizes patterned isotropic etching from the opposite side (exit side) of the nozzle to complete a passage through the membrane to the intermediate cross-section.

Although these prior art processes may provide satisfactory ink jet nozzle structures, both of the described processes and the resulting structures have inherent problems. For example, due to inherent wafer thickness variations and isotropic etch nonuniformities, these processes require extensive mechanical and/or chemical  
25 polishing of both major surfaces of the wafer to improve dimensional control of the resulting nozzle structures. This is a costly processing step. Additionally, the nozzle structures produced by these processes have heavily saturated p+ regions surrounding the exit openings, and these regions tend to be brittle and thus subject to failure when exposed to high fluid pressures or pressure transients typically present in ink jet printing systems.

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### Disclosure of Invention

In accordance with the present invention, a standard commercially available semi-conductor wafer of crystallographically oriented, monocrystalline p-type silicon is used to produce a single fluid nozzle or an array  
35 of nozzles directly and without the need for mechanical or chemical polishing of the two major surfaces of the wafer by a process wherein a low saturation n surface layer is formed on at least one major surface of the wafer. Materials resistant to an anisotropic etchant, later employed, are then deposited on both surfaces of the wafer. Thereafter, aperture masks defining the entrance and exit areas of a nozzle are formed on these major surfaces and the exit area is coated with a material which is both resistant to an etching solution and  
40 which provides an electrical connection to the n layer. A cavity is anisotropically etched from the entrance area of the wafer through to the n layer at the exit side by immersing the wafer in a caustic etching solution. A potential applied across the p/n junction at the exit side of the wafer electro-chemically stops the etching action leaving a membrane having a thickness substantially equal to the n-layer.

45 A passage is then anisotropically etched through the membrane from the exit side to complete the nozzle structure.

### The Drawings

50 Fig. 1 shows a perspective view of a portion of the nozzle structure in accordance with the present invention;

Fig. 2 is a cross-sectional view of the nozzle structure taken along line 2-2 of Fig.1 ;

Fig. 3 through 8 illustrate sequential cross-sectional views of a silicon wafer processed in accordance with the present invention.

### Detailed Description

In multi-nozzle ink jet printing systems utilizing nozzles made of semi-conductor material, some of the more important characteristics required of the nozzle are the uniformity in the size of each respective nozzle, spatial

distribution of the nozzles in an array, their resistance to cracking under the fluidic pressures encountered in the system, provision of an efficient mechanical impedance match between the fluid supply and the exit opening, as well as, their resistance to wear caused by the high velocity fluid flow through the nozzle structure.

Referring now to Fig. 1, there is shown a portion of the nozzle structure made in accordance with the present invention. Specifically a substrate 10 is shown having an array of uniform openings 11 therein. Each opening 11 starts with an initial, substantially square area and tapers to and terminates in a substantially square area smaller than the initial square area defining a membrane 12. As shown in Fig. 2, each membrane 12 in turn has an opening 13 extending therethrough which starts in a substantially square area smaller than the square area of each respective membrane 12 and terminates in a substantially square area larger than the starting square area of said opening. Both horizontal axes of the openings 13 in the membrane 12 are substantially aligned with the horizontal axes of each corresponding opening 11 in the main body of the wafer 10 by virtue of the wafer 10 crystallography.

Figs. 3 through 8 illustrate a sequence of process steps for production of an aperture in a single crystal silicon wafer 10 for forming one fluid nozzle or an array of nozzles. It is to be understood that the following process steps may be used in a different sequence and that other film materials for performing the same functions described below may be used. Furthermore, film formation, size, thickness and the like, may also be varied. The wafer 10 is of single crystal (100) oriented p type silicon with electrical resistivity of 0,5 to 100 ohm-cm, approximately 495  $\mu\text{m}$  to 515  $\mu\text{m}$  (19,5 to 20,5 mils) thick having front 14 and back 15 surfaces. The (100) planes are parallel to surfaces 14 and 15. As shown in Fig. 3, phosphorous is diffused into the front 14 and back 15 surfaces of the silicon wafer 10 to a depth of about 5  $\mu\text{m}$  forming n type layers 16 and 17. As will become obvious later only one diffused layer is required to form a nozzle structure by the process (exit side). The diffusion is accomplished in a well-known manner by having a gas mixture containing 0,75 %  $\text{PH}_3$ , 1 %  $\text{O}_2$ , and the make-up of Ar and  $\text{N}_2$  flow for 30 minutes past the silicon wafer 10 which is maintained at 950°C. This is followed by a long drive-in period (1050°C for 22 hours) to achieve a thick layer (about 5 microns). Since the final concentration of phosphorous in the n layers 16 and 17 is very low, this diffusion step introduces very little stress into the silicon wafer 10, and consequently the silicon structure retains its strength.

Next as shown in Fig. 4, both front 14 and back 15 surfaces of the wafer 10 are coated with a protective material such as LPCVD silicon nitride forming layers 18 and 19 which can resist a long etching period in a caustic (KOH) solution. One of the ways to accomplish this is to utilize a low pressure chemical vapor deposition of silicon nitride deposited at about 800°C. Oxide layers (not shown) less than 0,5  $\mu\text{m}$  thick may be grown on both sides of layers 18 and 19 to reduce the effect of stress between nitride and silicon and to improve adhesion of photoresist to nitride. To promote ease of photoshaping it is recommended that the wafer 10 when procured have its back surface 15 etched in an acidic rather than caustic solution.

Thereafter, masks are prepared corresponding to the desired entrance 20 and exit 21 areas of the nozzle. The masks for both entrance 20 and exit 21 areas are made circular in shape since the openings in the silicon wafer 10 defined by circular masks will etch out to squares parallel to the 100 planes, each square circumscribing its respective circle. Use of circular masks eliminates possible error due to the theta misalignment which may occur when a square shaped mask is used. The silicon nitride layers 18 and 19 are photoshaped simultaneously on both sides using a two-sided photospinner (not shown) and a two-sided aligner (not shown). The resulting structure after etching away of portions of layers 18 and 19 defining the entrance 20 and exit 21 areas, is shown in Fig. 5.

The exit area 21 is then protected from the etching solution by covering it with a metallic layer 22, as shown in Fig. 6, or by use of a hermetic mechanical fixture (not shown). Thereafter the wafer is submerged in a hot (80-85°C) KOH solution (not shown) and a potential is placed across the p/n junction at the back side 15 by connecting the positive side of an electrical power source (not shown) with the metallic layer 22 protecting the exit area 21. Other alkaline etch solutions such as metal hydroxides of the Group I-A elements of the Periodic Table, for example, NaOH,  $\text{NH}_4\text{OH}$ , or others, may be used. The use of electrochemically controlled thinning process for semi-conductors is well-known in the art and is described in detail in US-A-3,689,389.

The opening 11 in the monocrystalline silicon wafer 10 is etched anisotropically until the diffused layer 17 at the back side 25 is reached, at which time the etching action stops due to an oxide layer (not shown) which is caused to grow at the p/n junction due to the applied potential across the junction. It is well known in the art that the (111) plane is a slow etch plane in monocrystalline silicon material when a KOH etching solution is used. Thus, the etching step produces a pyramidal opening in the wafer 10 which opening truncates in a membrane 12 when it encounters the electrochemical etch barrier set up at the silicon and diffused layer 17 interface (p/n junction).

Thereafter, the wafer 10 is removed from the etching solution, the protective metallic layer 22 and associated electrical connection on the exit side are removed, and the entrance side 20 is protected from the etching solution usually by a layer 24 formed by air oxidation. The wafer 10 is then re-submersed into the etching

solution and a pyramidal passage is etched aniso-tropically from the back surface 15 to form the exit opening 13. The resulting structure is shown in Fig. 7.

5 If desired, the protective coatings 18, 19 and 24 are then removed leaving a completed pure silicon nozzle structure as shown in Fig. 8. Typically the initial opening of the entrance 20 is about 890  $\mu\text{m}$  (35 mils) wide and the smallest portion of the exit opening 13 is about 38  $\mu\text{m}$  to 102  $\mu\text{m}$  (1,5 to 4 mils) wide.

10 Since the etch rate perpendicular to the (111) planes is very low compared to the vertical etch rate (100), overetch does not mitigate against the high accuracy defined by the exit mask. To prevent ink from wetting the surface of the wafer on the exit side, the back surface 15 of the wafer 10 may be coated with a material of low surface energy such as Teflon.

## Claims

- 15 1. A nozzle comprising a nozzle body (10) formed of a monocrystalline p-type silicon material having a rectangular entrance aperture (11) of a first cross-sectional area which tapers to a second rectangular cross-sectional area which is smaller than the first cross-sectional area of said entrance aperture; and  
a membrane (12) of semi-conductor material formed within said second cross-sectional area and  
having an exit aperture;  
20 said membrane (12) being of  
n-type monocrystalline silicon having a thickness of 10 micrometers or less and has a rectangular exit aperture (13) therein, said exit aperture (13) having a first cross-sectional area which is smaller than the second cross-sectional area of the entrance aperture (11) and said exit aperture tapering from said  
25 second cross-sectional area of said entrance aperture to a second cross-sectional area of said exit aperture, said exit aperture first cross-sectional area being smaller than said second cross-sectional area thereof, said cross-sections being substantially parallel to the (100) planes of the monocrystalline silicon and said entrance and exit apertures being substantially concentric.
- 30 2. A process for forming a nozzle structure comprising an aperture in a section (10) of crystallographically oriented, p-type, monocrystalline silicon having first (15) and second (14) major surfaces;  
said process comprising the steps of  
forming a n surface layer (17) on the first major surface (15) of the silicon section (10);  
coating said first and second surfaces (14, 15) of the silicon section (10) with a material (18, 19)  
which resists etching;  
35 removing said coating from said first and second surfaces in the area (20, 21) defining the entrance (11) and exit (13) of the nozzle respectively;  
protecting the exit area (21) from the etching solution;  
establishing an electrochemical barrier at the silicon n layer interface;  
anisotropically etching a cavity from the second surface (14) of the silicon section to said n layer  
40 (17); and  
anisotropically etching a passage (13) through said n layer (17) from the first surface (15) of the silicon section (10).

## 45 Patentansprüche

1. Düse mit einem Düsenkörper (10), der aus einem monokristallinen p-Siliciummaterial geformt ist und der eine Eingangsöffnung (11) aufweist mit einer ersten rechteckigen Querschnittsfläche, die konisch zuläuft zu einer zweiten rechteckigen Querschnittsfläche, die kleiner ist als die erste Querschnittsfläche, und  
50 einer Membran (12) aus Halbleitermaterial, die in der zweiten Querschnittsfläche erzeugt ist und eine Ausgangsöffnung (13) aufweist,  
wobei die Membran (12) aus n-Silicium mit einer Dicke von 10 Mikrometer oder weniger besteht und eine rechteckige Ausgangsöffnung (13) besitzt,  
die Ausgangsöffnung (13) eine erste Querschnittsfläche aufweist, die kleiner ist als die zweite Querschnittsfläche der Eingangsöffnung (11),  
55 die Ausgangsöffnung (13) von der zweiten Querschnittsfläche der Eingangsöffnung zu einer zweiten Querschnittsfläche der Ausgangsöffnung konisch zuläuft,  
die erste Querschnittsfläche der Ausgangsöffnung kleiner als die zweite Querschnittsfläche der Ausgangsöffnung ist, die Querschnittsflächen im wesentlichen parallel zu den (100)-Ebenen des monokri-

stallinen Siliciums verlaufen, und die Eingangs- und Ausgangsöffnung im wesentlichen konzentrisch sind.

- 5 2. Verfahren zur Herstellung einer Düsenstruktur, die eine Öffnung in einem Abschnitt (10) aus kristallographisch orientiertem, monokristallinem p-Silicium mit einer ersten (15) und einer zweiten (14) Hauptfläche enthält,  
mit den Verfahrensschritten:  
Herstellen einer n-Oberflächenschicht (17) auf der ersten Hauptfläche (15) des Siliciumabschnitts (10);  
10 Beschichten der ersten und zweiten Hauptfläche (14, 15) des Siliciumabschnitts (10) mit einem gegen Ätzen beständigen Material (18, 19);  
Entfernen der Beschichtung von der ersten und zweiten Hauptfläche in den Bereichen (20, 21), die den Eingang (11) bzw. Ausgang (13) der Düse definieren;  
Schützen des Ausgangsbereiches (21) vor der Ätzlösung; Herstellen einer elektrochemischen Barriere  
15 an der n-Schicht-Grenzfläche,  
anisotropes Ätzen eines Hohlraumes (11), ausgehend von der zweiten Hauptfläche (14) des Siliciumabschnitts bis zu der n-Schicht (17); und  
anisotropes Ätzen einer Öffnung (13) durch die n-Schicht (17) von der ersten Hauptfläche (15) des Siliciumabschnitts (10) aus.

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## Revendications

- 25 1. Buse comprenant un corps (10) de buse formé d'une matière du type silicium monocristallin de type p présentant une ouverture d'entrée rectangulaire (11) d'une première coupe transversale qui s'effile jusqu'à une seconde coupe transversale rectangulaire qui est plus petite que la première coupe transversale de ladite ouverture d'entrée ; et  
une membrane (12) en matière semi-conductrice formée à l'intérieur de ladite seconde coupe transversale et ayant une ouverture de sortie ;  
30 ladite membrane (12) étant en silicium mono-cristallin de type n ayant une épaisseur de 10 micromètres ou moins et présentant une ouverture rectangulaire (13) de sortie, ladite ouverture (13) de sortie ayant une première coupe transversale qui est plus petite que la seconde coupe transversale de l'ouverture d'entrée (11) et ladite ouverture de sortie s'amincissant de ladite seconde coupe transversale de ladite ouverture d'entrée jusqu'à une seconde coupe transversale de ladite ouverture de sortie, ladite  
35 première coupe transversale de l'ouverture de sortie étant plus petite que sa seconde coupe transversale, lesdites coupes transversales étant sensiblement parallèles aux plans (100) du silicium monocristallin et lesdites ouvertures d'entrée et de sortie étant sensiblement concentriques.
- 40 2. Procédé pour former une structure de buse comprenant une ouverture dans une partie (10) de silicium monocristallin de type p, à orientation cristallographique, présentant des première (15) et seconde (14) surfaces principales ;  
ledit procédé comprenant les étapes qui consistent  
à former une couche superficielle n (17) sur la première surface principale (15) de la partie (10) en silicium ;  
45 à revêtir lesdites première et seconde surfaces (14, 15) de la partie (10) en silicium d'une matière (18, 19) qui résiste à la gravure ;  
à enlever ledit revêtement desdites première et seconde surfaces dans la section (20, 21) définissant l'entrée (11) et la sortie (13) de la buse, respectivement ;  
à protéger la section de sortie (21) de la solution de gravure ;  
50 à établir une couche d'arrêt électrochimique à l'interface du silicium et de la couche n ;  
à graver de façon anisotrope une cavité depuis la seconde surface (14) de la partie en silicium jusqu'à ladite couche n (17) ; et  
à graver de façon anisotrope un passage (13) à travers ladite couche n (17) depuis la première surface (15) de la partie (10) en silicium.

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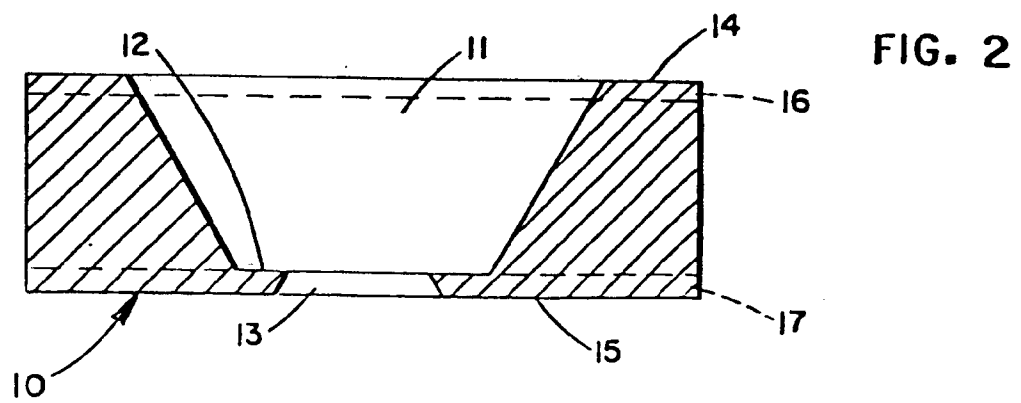
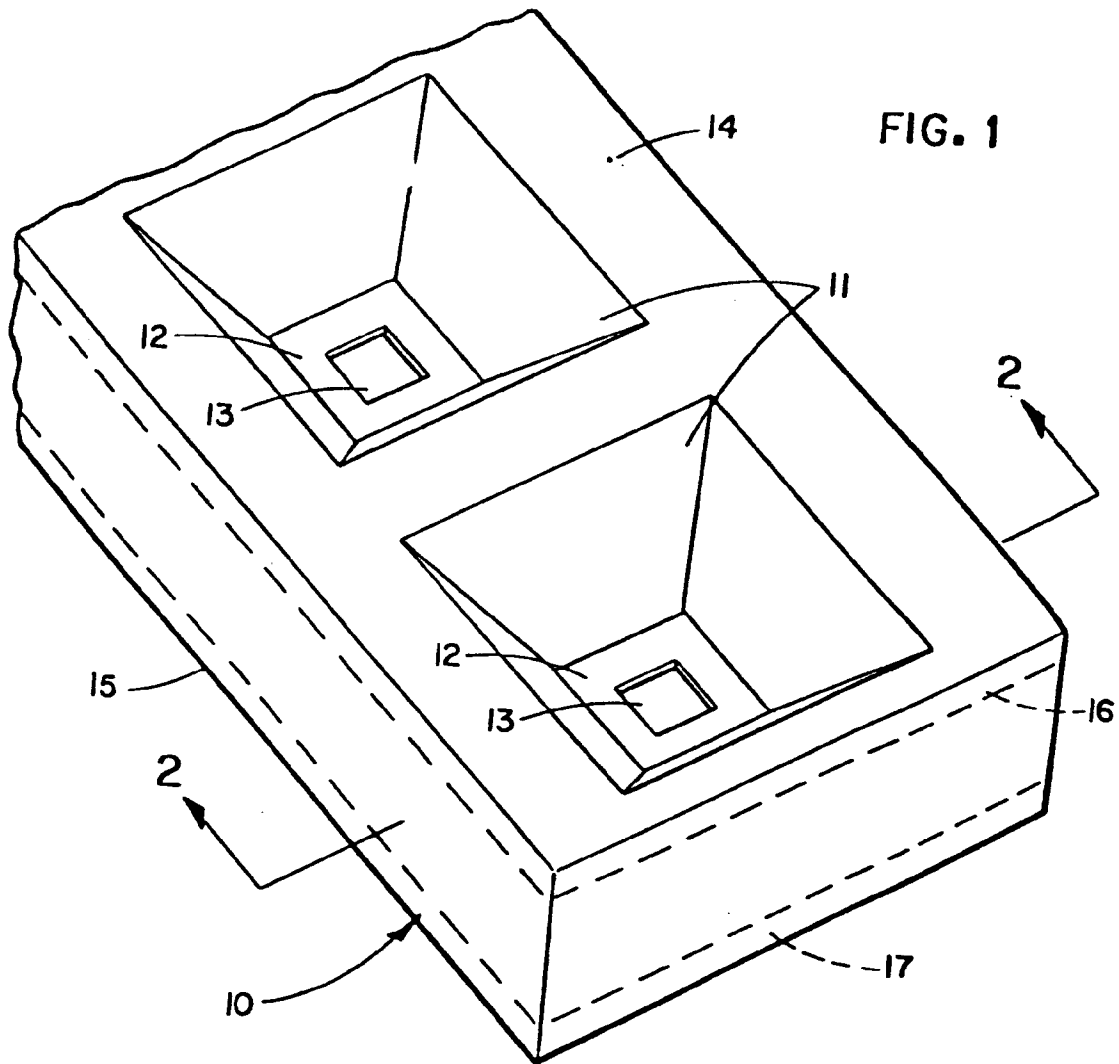


FIG. 3

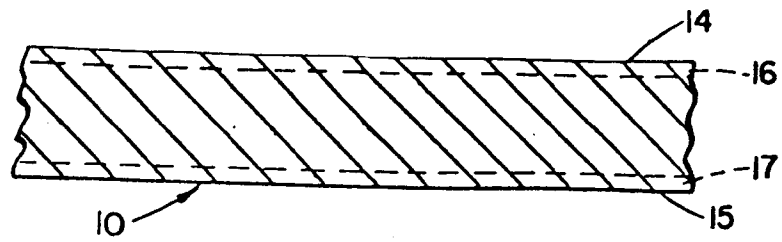


FIG. 4

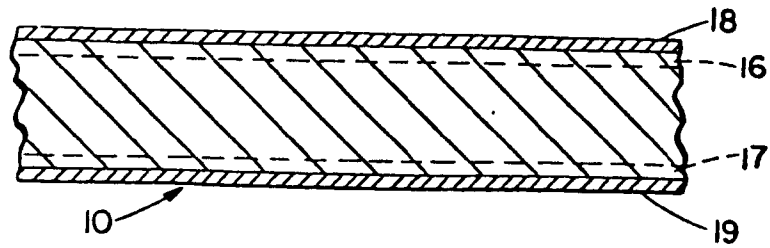


FIG. 5

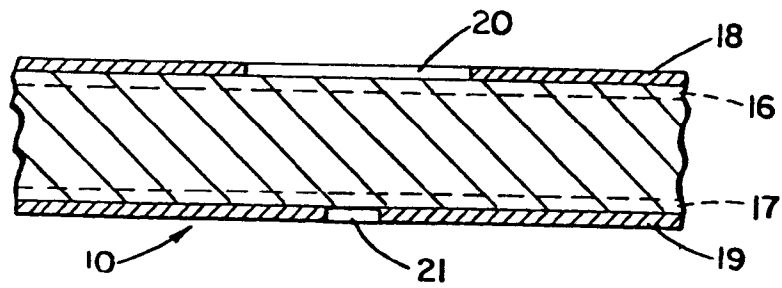


FIG. 6

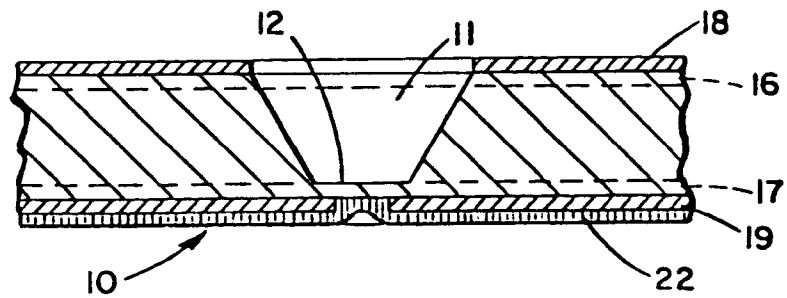


FIG. 7

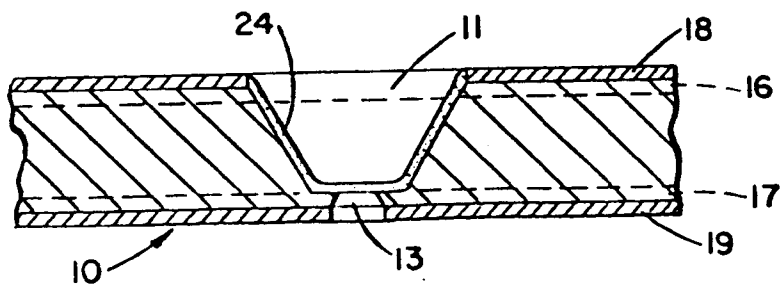


FIG. 8

